Quaternary Carbon Synthesis via Lewis Base Reductive Aldol:
Mechanistic Calculations and Application towards *isopalhinine A* Core Synthesis

by

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## DEDICATION

I dedicate this thesis to my parents, Kris, my sister Alex, my dog Max, old and new friends, extended family, mentors, and coworkers.

**ACKNOWLEDGMENTS**

I would like to thank my professor Dr. Corinna Schindler, for being an exceptionally excellent chemist, and for always being supportive and dedicated to the lab. I thank my committee members Corey Stephenson, Melanie Sanford, and Amanda Garner, for being encouraging and capable of meeting, showing interest in my projects and for their helpful advice with edits. I would also like to thank Paul Zimmerman and Amanda Dewyer, for meeting with me often and teaching me how to understand and use computations. I'd especially like to thank everyone in the Schindler lab.

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| | |
|---|---|
| δ | chemical shift, delta |
| $\tau_5$ | geometry index |
| µM | micromolar |
| A-549 | adenocarcinomic human alveolar basal epithelial cells |
| AChE | acetylcholinesterase |
| AIBN | azobisisobutyronitrile |
| $AlCl_3$ | aluminum trichlroide, aluminum (III) chloride |
| BChE | butyrylcholinesterase |
| $BF_3$ | boron trifluoride |
| Bn | benzyl |
| Boc | tert-butyloxycarbonyl protecting group |
| $Boc_2O$ | di-tert-butyl dicarbonate, Boc anhydride |
| $Bu_3SnH$ | tributyltin hydride |
| °C | degree Celsius |
| C20 | twenty carbon units |
| cat. | catalytic |
| C-C | carbon-carbon bond |
| $CDCl_3$ | deuterated chloroform, chroroform-d |
| $CeCl_3$ | cerium trichlroride, cerium (III) chloride |
| C-H | carbon-hydrogen bond |
| $CH_2N_2$ | diazomethane |
| $-CH_3$ | methyl group |
| CHO | aldehyde functional group |
| Cl | chlorine, chloride |
| $cm^{-1}$ | wavenumber |
| C=O | carbonyl group |
| $CO_2$ | carbon dioxide |
| $CO_2Me$ | methyl ester |
| $CO_2H$ | carboxylic acid |
| CoA | coenzyme A |
| CuAO | Copper-containing amine oxidase |
| D | deuterium |
| DA | Diels Alder [4+2] cycloaddition |
| DBU | 1,8-diazabicyclo(5.4.0)undec-7-ene |
| DCC | N, N'-dicyclohexylcarbodiimide |
| DCE | 1,2-dichloroethane |
| DCM | dichloromethane, methylene chloride |
| dd | doublet of doublets |
| ddd | doublet of doublet of doublets |

| | |
|---|---|
| DFT | density functional theory |
| DIPEA, DIEA | N,N-diisopropylethyl amide, Hünig's base |
| DMAP | 4-dimethylaminopyridine |
| DMP | Dess-Martin periodinane |
| DNA | deoxyribonucleic acid |
| d.r. | diastereomeric ratio |
| dt | doublet of triplets |
| EDC-HCl | N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride |
| *ent*-CPP | enantiomer of copalyl diphosphate |
| equiv. | equivalents |
| ESI | electrospray ionization |
| Et | ethyl |
| $Et_3N$, TEA | N,N-diethylethanamide, triethylamine |
| $Et_2O$ | ether, diethyl ether |
| EtOAc | ethyl acetate |
| EtOH | ethanol |
| Fe(PDP) | White-Chen catalyst |
| FT-IR | Fourier transform infrared spectroscopy |
| g | grams |
| GGPP | geranylgeranyl pyrophosphate |
| GSM | growing string method |
| h | hours |
| H, $H^+$, and $H^-$ | hydrogen, proton, and hydride |
| [+$H_2$] | hydrogenation |
| $H_2O_2$ | hydrogen peroxide |
| HCHO | formaldehyde |
| HCl | hydrochloric acid |
| HL-60 | human promyelocytic leukemia cells |
| HMPA | hexamethylphosphoramide |
| HOMO | highest occupied molecular orbital |
| HRMS | high-resolution mass spectrometry |
| $HSiCl_3$ | trichlorosilane |
| Hz | Hertz |
| $(Ipc)_2BH$ | Diisopinocampheylborane |
| *i*Pr | Isopropyl |
| kcal, kcal/mol | kilocalorie, kilocalories per mole |
| $K_2CO_3$ | potassium carbonate |
| K562 | chronic myelogenous leukemia cells |
| $KMnO_4$ | potassium permanganate |
| L | liters |
| LAH, $LiAlH_4$ | lithium aluminum hydride |
| LB | Lewis base |
| LDA | lithium diisopropylamide |
| Li | lithium |
| LiHMDS, $LiN(SiMe_3)_2$ | lithium bis(trimethylsilyl)amide |
| LUMO | lowest unoccupied molecular orbital |

| | |
|---|---|
| m | multiplet |
| MCF-7 | Michigan Cancer Foundation-7, breast cancer cell line |
| *m*CPBA | *meta*-chloroperoxybenzoic acid |
| -Me | methyl functional group |
| $MeNO_2$ | nitromethane |
| MeOH | methanol |
| MHz | megahertz |
| $MnO_2$ | manganese dioxide, manganese (IV) oxide |
| mol | mole |
| MOM | methoxymethyl acetal |
| N | nitrogen |
| Na | sodium |
| $NaBH_4$ | sodium borohydride |
| NaH | sodium Hydride |
| $NaHCO_3$ | sodium bicarbonate |
| NaOAc | sodium acetate |
| NCMe, $CH_3CN$ | acetonitrile |
| $N_2H_4$-$H_2O$ | hydrazine hydrate |
| NF-κB | nuclear factor kappa-light-chain-enhancer of activated B cells |
| $NH_3$ | ammonia |
| NMR | nuclear magnetic resonance |
| $NO_2$ | nitro functional group |
| NPhth | phthalimide, 1,3-dihydro-1,3-dioxoisoindole |
| $NR_2$ | protected amine |
| O | oxygen |
| [O] | oxidation |
| OH | hydroxyl, alcohol |
| OMe | methoxy |
| *o*-OMe-TPPO | Tris(2-methoxyphenyl)phosphine oxide |
| *o,p*-diOMe-TPPO | Tris(2,4-dimethoxyphenyl)phosphine oxide |
| -OR | protected alcohol |
| OTBDPS | *tert*-butyldimethylsilyl ether |
| O=P, P=O | phosphine oxide |
| O-Si-O | oxygen-silicon-oxygen angle/geometry |
| Pd/C | Palladium on carbon (activated charcoal) |
| $Pd(OH)_2/C$ | Pearlman's catalyst, palladium hydroxide on carbon |
| Ph | phenyl |
| PhCHO | benzaldehyde |
| PIFA, $PhI(OCOCF_3)_2$ | (Bis(trifluoroacetoxy)iodo)benzene |
| PMP | para-methoxyphenyl |
| *p*-$NMe_2$-TPPO | Tris(4-dimethylaminophenyl)phosphine oxide |
| $POCl_3$ | Phosphoryl chloride, phosphorus oxychloride |
| *p*-OMe-TPPO | Tris(4-methoxyphenyl)phosphine oxide |
| $R_f$ | retention factor |
| rt | room temperature |

| | |
|---|---|
| s | singlet |
| $SbF_6$ | hexafluoroantimonate |
| SE-GSM | single-ended growing string method |
| Si | silicon |
| Si-O | silicon oxygen bond |
| $SmI_2$ | Samarium (II) iodide, Kagan's reagent |
| SMMC-7721 | human hepatoma cells |
| SW-480 | human colon adenocarcinoma cells |
| t | triplet |
| TBAF | tetra-*n*-butylammonium fluoride |
| TBDPS, TBS | *tert*-butyldiphenylsilyl |
| *t*-BuLi | *tert*-butyllithium |
| *t*-BuOH | *tert*-butanol |
| TCI | Tokyo Chemical Industry |
| td | triplet of doublets |
| THF | tetrahydrofuran, oxolane |
| TLC | thin layer chromatography |
| TMS | trimethylsilyl |
| TPPO | triphenylphosphine oxide |
| TS | transition state |
| TsN | 4-toluenesulfonamide |
| TsO | tosyl, $CH_3C_6H_4SO_2$ |
| TsOH | para-toluenesulfonic acid |
| tt | triplet of triplets |
| W | watts |

## ABSTRACT

To synthesize palhinine alkaloids, a quaternary reductive aldol reaction was used to generate rapid stereochemical complexity from simple building blocks. This approach, which can also be used for diterpene synthesis, couples an asymmetric Diels Alder adduct with a N-containing aldehyde fragment while also generating an alcohol stereocenter. In subsequent steps, this intermediate is hydrogenated and isomerized into a cage-like structure through protecting group manipulation. This core has the prospective to be elaborated into the natural product isopalhinine A.

In particular, the reductive aldol reaction was examined with a variety of substrates and catalysts, experimentally and computationally. The electron-rich tris(4-methoxyphenyl)phosphine oxide was used as a Lewis base catalyst capable of promoting both reduction and aldol. This catalyst was effective for a variety of substrates including lactones, lactams, and morpholine amides, which were coupled with aldehydes to generate quaternary aldol fragments. For several examples, a mixture of diastereomers is generated, and this stereochemistry was verified by X-ray crystallography.

To model this reaction, DFT, Zstruct, and GSM were used to study the mechanisms of reduction, catalyst placement, and aldol for a variety of substrates and catalysts. Interestingly, it was found that reduction results in a trigonal bipyramidal Si complex with both catalyst and substrate equatorial, approximately 120° apart. According to DFT, axial catalyst and equatorial substrate placement, separated by approximately 90°, is the most stable conformation. However, for the aldol step, both ligands are axial, separated by approximately 180° to accommodate the incoming aldehyde partner. These isomers could interconvert through a Berry mechanism or by a stepwise dissociation and re-coordination. These DFT and TS structures set the stage for the goal of developing stronger and more selective Lewis base catalysts.

## CHAPTER I: Anti-inflammatory NF-kB inhibitors and the importance of method development

*Abstract*

This chapter summarizes the background of our synthesis target, isopalhinine A, as well as goals of our research in relation to this target. In addition to the synthesis of possible anti-inflammatory natural products, method development and mechanistic understanding are equally important goals of this research. Delving into a method experimentally and theoretically can facilitate broader applicability of substrates and also create a clearer picture of the mechanistic details. From these ideas, a method's limitations can be understood and particular variations can be developed.

*Cancer and Inflammation*

In people and animals, inflammation is linked with activation of the NF-κB signaling pathway (Figure 1.1).[1] This protein-signaling complex serves a role in animal cell survival mechanisms. "Nuclear translocation of activated NF-kB complex induces transcription of anti-apoptotic genes."[2] This pathway is predominantly inactive during normal physiological conditions and is activated when cells are exposed to mutagens[3] for the purpose of repairing DNA damage and preventing cell death. Additionally, it can be over-active and aberrant in cancerous cells.[4] Responsive activity of this signaling pathway is a standard and normal part of immune defense, but if a tumor is present, causing systemic inflammation, this pathway may be over-active, and this exacerbates cancerous cell growth by preventing apoptosis of cancer cells. This counteracts treatment regimens aimed at killing cancer cells.[5] An over-active inflammatory chemical response causes more random mutations leading to the growth of cancerous cells, which themselves generate more inflammatory molecules, which further mutate healthy cells to cancerous cells.

Several types of cancers have been linked to abnormal NF-κB regulation including breast, prostate, renal, bladder, pancreatic, colon, and ovarian cancers. Standard cancer therapies target tumor cells, killing dividing cells by using small molecules to arrest the cell cycle. This

type of treatment is not always effective because multidrug resistance can occur. In response to chemotherapeutic drugs, the cancerous cells express efflux pumps,[6] pushing out the chemotherapeutic agents. It has been shown that cancerous cells with active NF-κB have a greater survival rate during chemotherapy,[7] which blocks effective treatment. Cancer therapy targeting both the tumor and the inflammation of the surrounding non-cancerous tissues would be beneficial because cancer-related deaths are often due to an underlying inflammatory or immune response. More than 700 inhibitors of NF-κB are known. However, few of them directly target the transcription factor itself, and this results in off-target effects. There is a need to synthesize small molecule inhibitors that more directly inhibit NF-κB p50 subunit.

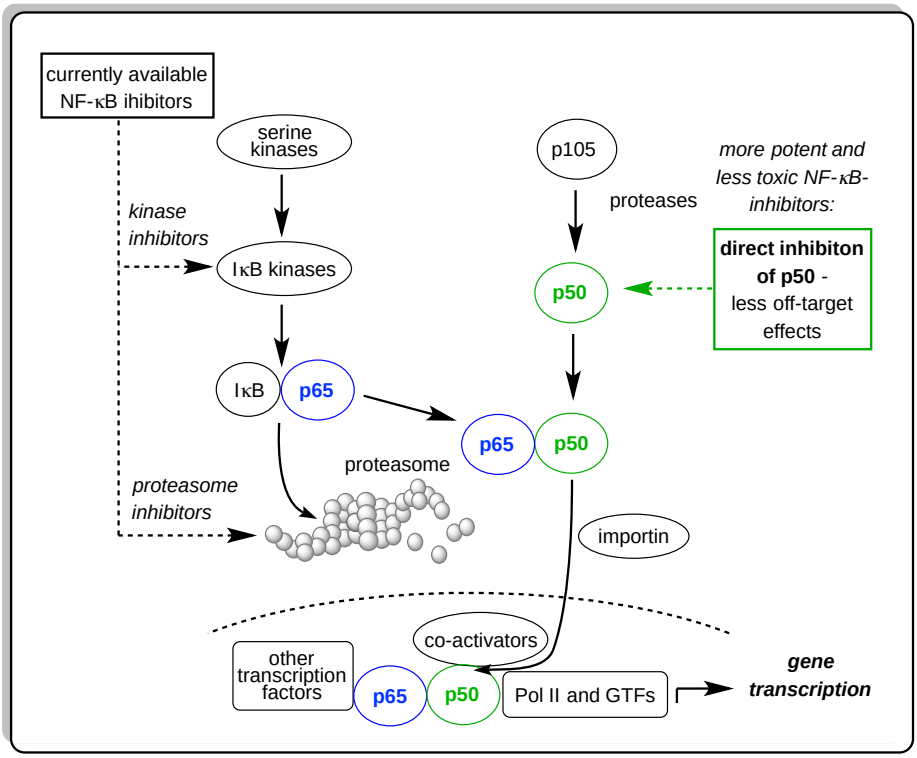



Figure 1.1 The NF-κB protein complex, found in animal cells, is a key regulator of cell proliferation and survival. Many cancerous and chronically inflamed cells have over-active NF-κB. There is a need to develop more potent and less toxic NF-κB inhibitors by directly targeting the p50 subunit.

*A New Lab: New Methods*

With the objective to efficiently synthesize selective NF-κB-inhibiting molecules, the Schindler lab began in the summer of 2013. In addition to the direct goal of gaining access to small molecule NF-κB inhibitors, a supplementary and equally significant goal of this research is

to develop new synthetic methods that can replace existing approaches limited by their toxicity and generation of excess chemical waste.

For developing a drug to treat a worldwide disease, it is ideal to have a way of manufacturing the drug that can be scaled to global magnitudes without environmentally harmful consequences.[8] In a medicinal chemistry investigation, the target structure could be obtained by any means necessary, less limited by cost and scalability, as the most important aspect at that stage is the molecule itself, and how its structure can be altered to design a structure that has the best potency and drug properties.[9] Later on, once a molecule is chosen as the most effective structure, and larger amounts are needed for clinical trials, the synthesis may need to be re-designed by process chemists to satisfy environmental and budget considerations.[10] The more environmentally sound and robust the original medicinal chemistry method was, the less effort will be required to create new routes or optimizations. Better methods can prevent fewer setbacks along the drug development pipeline,[11] providing improved access to lifesaving drugs.[12]

*Fe(III)-catalyzed COM*

Some of the most groundbreaking work centers on developing new methods that use catalytic amounts of environmentally benign and inexpensive catalysts.[13] In 2016, the Schindler lab reported a carbonyl-olefin metathesis reaction catalyzed by Iron(III) Lewis acids.[14] This transformation has typically been conducted as a two-step process involving: 1) a photochemical reaction between a carbonyl and an olefin to generate an oxetane, commonly referred to as the Paterno-Buchi reaction, and then 2) fragmentation of the oxetane using heat, acidic, or basic conditions.[15] This can be problematic, as the conditions required to fragment the oxetane may destroy sensitive functional groups on a molecule. More direct one-step methods for carbonyl-olefin metathesis involve organometallic complexes containing Molybdenum[16] or Titanium. Organo-catalysts have also been used, however these examples are more specific to highly strained substrates and are not generally applicable.[17]

*New Synthetic Methods for Complex Molecules*

A broad but guided approach for developing new synthetic methods is used, as outlined in Figure 1.2. The goal is to permit intricate target molecules, which would otherwise require multiple steps to make, to be straightforwardly synthesized[18] and tested for biological activity. Other than expediting the synthesis of a chosen structure, the methods themselves can have an

impact on collective organic chemistry practices. A new method is robust if it can be easily scaled, and economically sensible methods should use less expensive or toxic reagents compared to what was available beforehand.[19] If a method is safe, general and consistent, it will be more likely to be adapted by the scientific community and used practically by chemists.

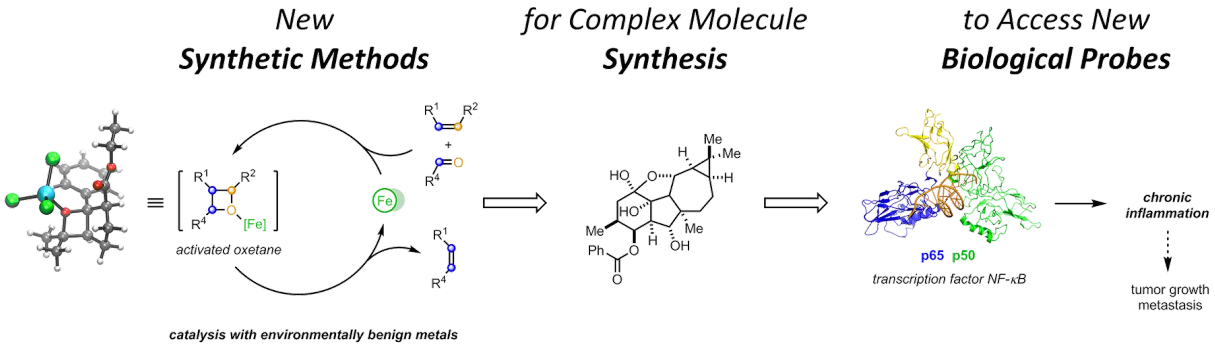



Figure 1.2. Research strategies and goals of the Schindler lab: a) the development of new, environmentally benign synthetic methods. b) Synthesis of natural product targets and analogues, and c) evaluation of molecules regarding their ability to inhibit NF-κB to treat cancer and inflammation.

Method development is only limited by one's imagination, but creating such methods is not straightforward. The process requires in-depth understanding of existing protocols, an idea for innovation, an indefinite amount of hypothesis-driven trial and error, and also a good amount of serendipity or luck.[20] From an initial novel reaction hit, thorough screening and optimization for the best reaction conditions is necessary as a control. Further pursuits could include the synthesis of a diverse set of substrates for applied purposes,[21] investigation of reactivity on altered substrates,[22] or mechanistic investigations.[23] The knowledge obtained from these studies is invaluable. As a beginning research group, the lab has been exploring method development as a goal for many projects, and the ultimate purpose is to apply these new transformations to the rapid synthesis of natural products.[24] In the interim, in order to establish vigorous and reliable biochemical methods for testing NF-*k*B inhibitors, we also have the capability to expeditiously access new biological probes from the scaffolds of easily attainable complex molecules.[25]

*Potent and Selective NF-kB inhibitors*

The diterpene gibberellic acid is structurally complex, containing multiple fused rings and stereocenters, but fortunately it is fairly inexpensive for natural product synthesis purposes, (Sigma Aldrich, $30/g) as it is a common agricultural chemical that is used for farming. It is produced by plants and fungi as a growth hormone, and can be manufactured by fermentation.[26]

Angela Koehler was the first to demonstrate that the plant hormone gibberellic acid is a selective NF-κB inhibitor with no observed cytotoxicity.[27] Based on this initial activity and the structure of gibberellic acid, it was hypothesized that better and stronger inhibitors could be rationally designed by improving the lipophilicity, cell permeability, and stability of these molecules. It has been shown that the gibberellic acid OMe ketone (Figure 1.3), which can be made in two steps from gibberellic acid, shows 100% inhibition against NF-κB luciferase at a concentration of 10 μM. This molecule was obtained by James Annand en-route to pharbinilic acid; the first isolated naturally occurring allogibberic acid. These promising results encourage us to synthesize more natural product scaffolds, (Figure 1.3) so that we can elucidate the structural-activity relationships of these molecules with NF-κB.

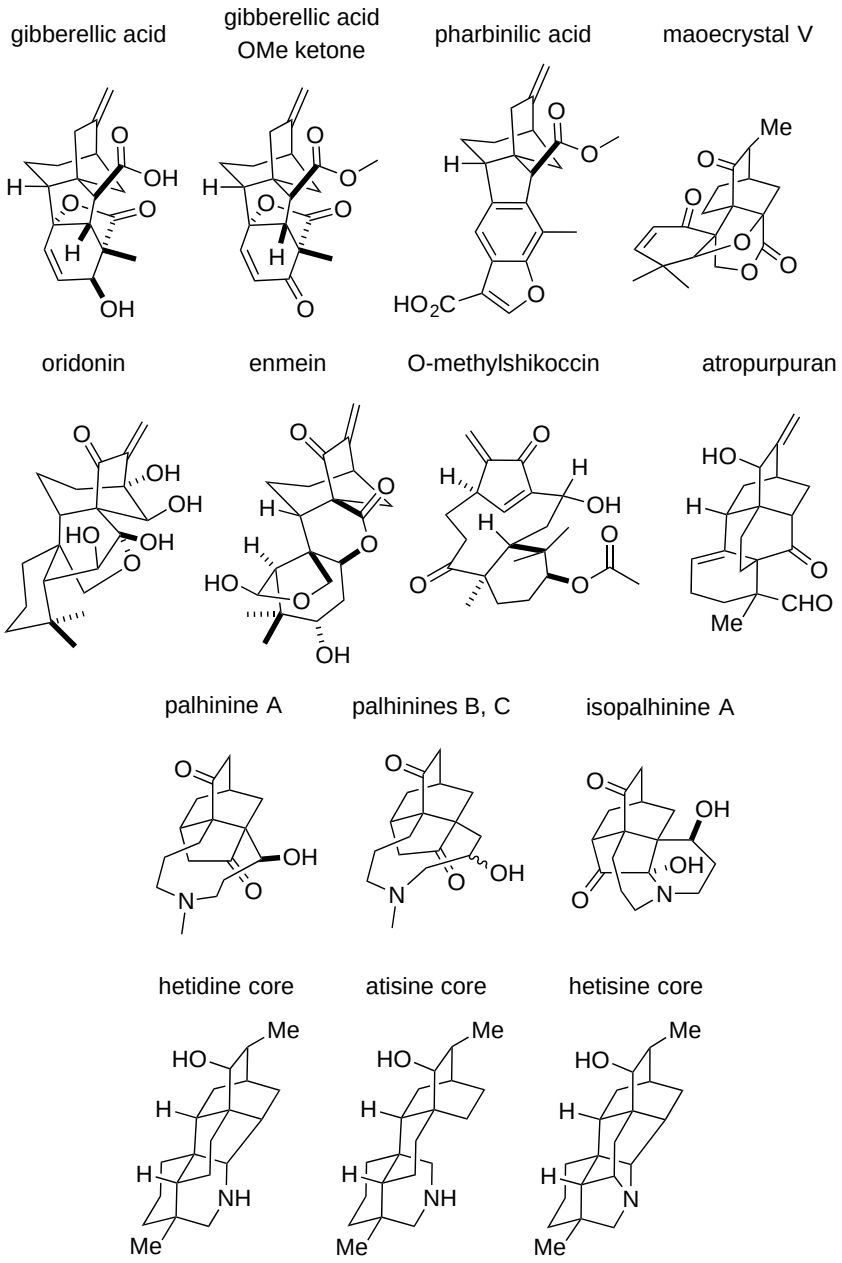



Figure 1.3. A selection of diterpenoid and alkaloid synthetic targets.

*Diterpenoids and other cage-like Gibberellin Structural Analogs*

Gibberellic acid and pharbinilic acid belong to a larger category of molecules known as the *ent*-kaurene diterpenoids,[28] consisting of C20 tetracyclic building blocks (Figure 1.4). Diterpene scaffolds arise from the precursor GGPP (geranylgeranyl pyrophosphate), which is composed of four 5C isoprene units. For the *ent*-kaurenes, GGPP is cyclized to the di-cyclohexyl unit *ent*-CPP by (+)-copalyl diphosphate synthase, and then this precursor is converted to a

tetracyclic scaffold by *ent*-kaurene synthase, which controls carbocation shifts to establish the core. Subsequent *ent*-kaurene oxidases and hydroxylases decorate the scaffold with alcohol and ketone substituents at various positions. Additional ring opening and closing reactions can occur, and there are five major classes of *ent*-kaurenes according to these connectivity groups. As presented in Figure 1.3, gibberellic acid and its *ent*-kaurene relatives maoecrystal V, oridonin, enmein, and O-methylshikoccin are architecturally "not flat" molecules, in particular the northern portion of the molecule, which contains a fused 5-6-7 bicycle. These three-dimensional characteristics make them highly attractive synthetic targets compared to achiral, aromatic compounds.[29]

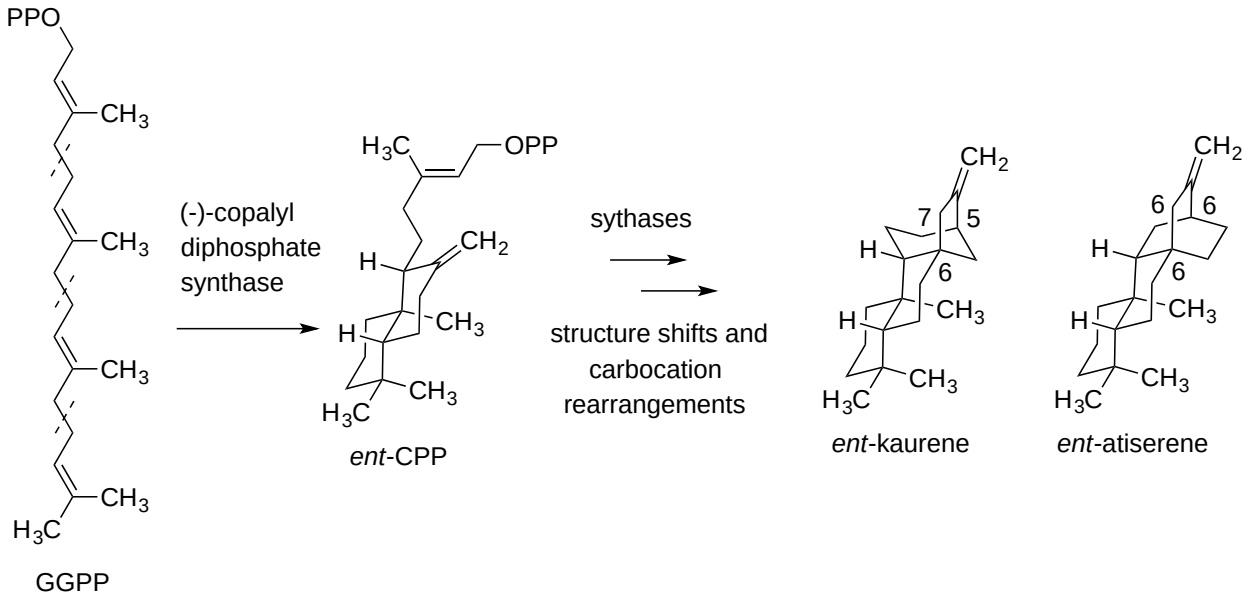



Figure 1.4 The shared biosynthetic pathway of *ent*-kaurene and *ent*-atiserene diterpenoids.

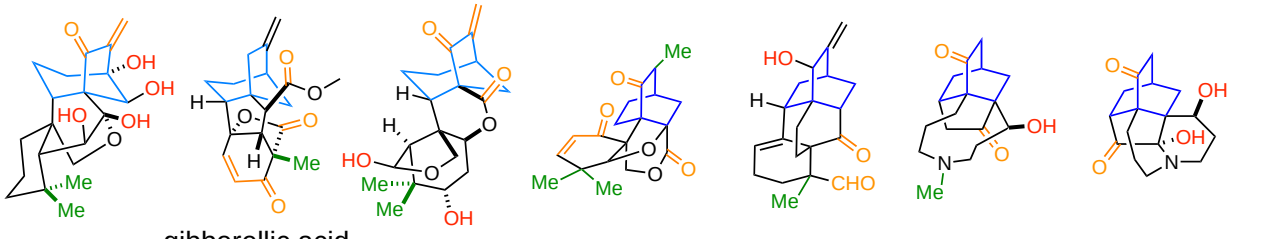
The *ent*-kaurenes are only a small portion of the many diterpenes isolated from medicinal plants. Carbocation shifts result in a wide variety of structures. In the diterpene family, the atiserenes contain a 6-6-6 fused bicycle as opposed to the 5-6-7 bicycles seen in kaurenes (Figure 1.4). Atropourpuran, the hetidines, atisines, and hetisines are all polyclic C20 diterpenoids, derived from *ent*-atiserene, that have been described as having a cage-like structure (Figure 1.3). They have been isolated from *Aconitum* plants, which are generally toxic, but do have a long history of use for a variety of ailments.[30] Because these plants are used homeopathically, and

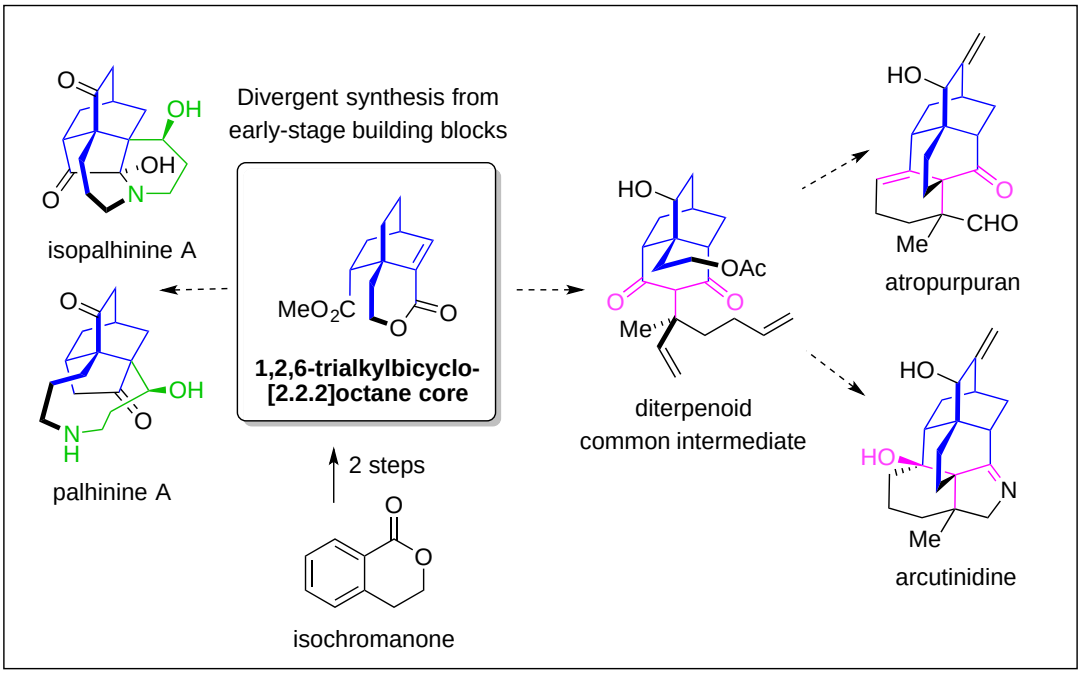
also considering the shared biosynthetic route with the gibberellins, we aim to gain access to these molecules in order to test them for NF-kB inhibition.

*New Targets: New Approaches*

Some privileged scaffolds such as the gibberellins are readily available, and for these occasions semisynthetic methods are cost-effective and practical. However, many structures that are discovered from nature are the result of long and intricate biosynthetic pathways that produce complex mixtures of molecules in scarce quantities that are unrecognizable from their building blocks (Figure 1.6).[31] The ability of enzymes to rapidly construct and selectively functionalize a molecule cannot easily be reproduced using standard organic chemistry techniques. Furthermore, many natural products come from plants and other organisms that can only thrive and produce these preferred molecules in their natural habitat,[32] so using enzymatic synthesis, either by the whole plant or specific enzymes, is not easily achievable.

There is not always an existing molecular scaffold that can be obtained and then manipulated to garner a rare and unique target.[33] Consequently, the lab develops core-building methods that can overcome current synthetic limitations.[34] Yong Qin and coworkers recently reported the first total synthesis of atropurpuran starting from a single aromatic ring building block precursor.[35] Our lab's strategy to these targets also begins with commercially available, simple building blocks. Additionally, during our search for related synthetic targets and strategies, we noticed that the palhinine alkaloids,[36] specifically palhinines A-C and isopalhinine A also contained this 6-6-6-fused bicyclic motif (Figure 1.3). From this assessment, we developed a synthetic route to the palhinines that diverges from our atropurpuran strategy (Figure 1.5).






Development and/or adaptation of new synthetic methods

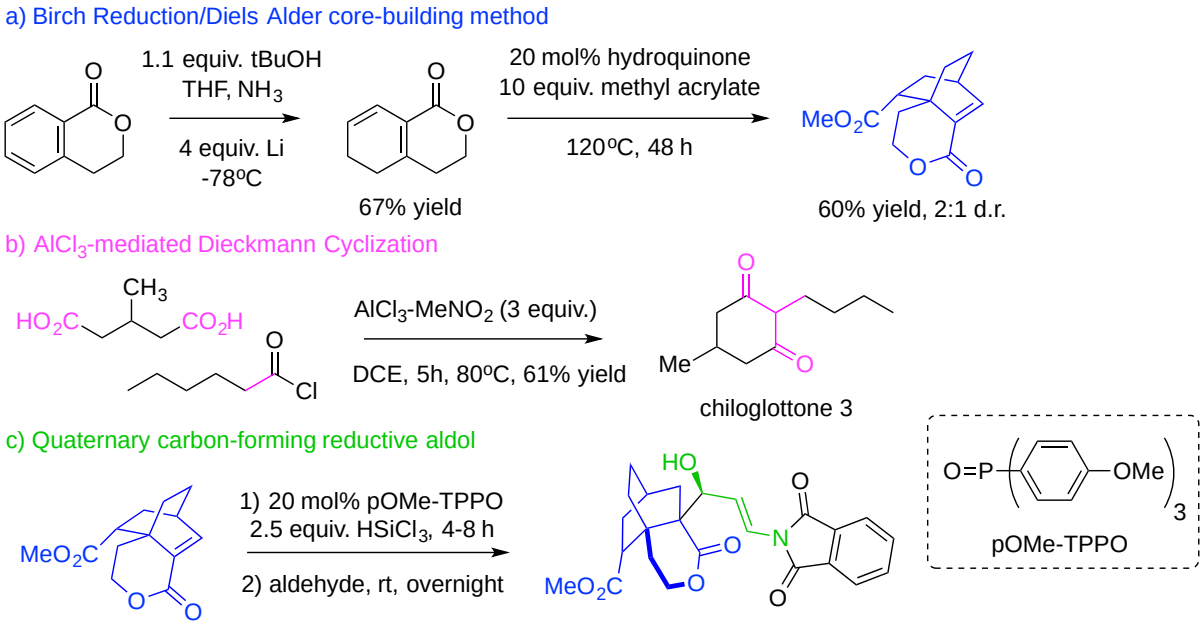



Figure 1.5 A divergent synthetic strategy for accessing the ent-atiserene structures as well as the palhinine alkaloids from isochromanone by developing new methods: a) a rapid construction of shared bicyclic core, b) Dieckmann cyclization to create cage-like motifs, c) Reductive aldol for the formation of quaternary carbons and alcohol stereocenters.

*Quaternary-forming reaction on a lactone to build isopalhinine A*

The natural products isopalhinine A, palhinine A, maoecrystal V, and atropurpuran all contain a 1,2,6-trialkylbicyclo[2.2.2]octane core, which is also present in a large number of biologically active diterpenoids such as the hetidines, atisines, and hetisines. The lycopodium alkaloid isopalhinine A was isolated from the club moss *Palhinhaea cernua*, which has been used to treat inflammation. Specifically, this work concerns the synthesis of the alkaloid isopalhinine A. In detail, this thesis discusses:

a) Chapter II: Total Synthesis. The synthesis of a 6-6-6 bicyclic scaffold from a sequence involving a Birch reduction, isomerization, Diels-Alder, reductive aldol, and lactam-lactone cascade. This precursor contains all necessary stereochemistry present in isopalhinine A.
b) Chapter III: Method development. A Lewis base-catalyzed reductive aldol reaction for the formation of quaternary stereocenters. This method was utilized for the isopalhinine A scaffold, as well as applied to a general set of heterocyclic substrates.
c) Chapter IV: Mechanistic evaluation of the reductive aldol reaction computationally: DFT calculations and growing string methods. Modeled transition states can explain discrepancies in reactivity for different catalysts and substrates.

*Isopalhinine A biosynthesis from Palhinhaea cernua L*

The palhinine alkaloids contain structural similarities to diterpenes, however they are coincidental, as these target molecules have a distinct biosynthetic pathway. When these structures were first elucidated in 1956, Conroy proposed that the alkaloids could be derived from “two eight carbon polyacetate straight chains…two molecules of a 3,5,7-triketooctanoic acid equivalent”.[37] Although the exact mechanism was unknown at the time, Conroy was essentially correct that there was some kind of dimerization event of two smaller units to construct the core. Extensive isotope-labeling studies by Thomas Hemscheidt and coworkers have evidenced biosynthetic mechanisms arising from the precursors lysine and acetyl CoA.[38] These investigations were conducted in the field to prove these exact precursors and mechanisms.

Studies have since proven the exact structure of these two units that come together to form the principal atoms: 4-(2-piperidyl) acetoacetate and pelleteirine, and they both come from lysine and acetate-derived precursors. To begin, lysine is enzymatically decarboxylated and then oxidized to the precursor δ-amino pentanal, which then cyclizes to the imine Δ1-piperidine.[39] This highly electrophilic intermediate undergoes a Mannich-type condensation with 3-oxoglutaric acid, derived from acetyl CoA (Figure 1.6). A single decarboxylation produces the building block 4-(2-piperidyl) acetoacetate, and then a second decarboxylation yields the other partner, pelleteirine.[40] These precursors combine to form the backbone common to typical lycopodium alkaloids. The palhinines are generated from this basis followed by many structural-changing rearrangements, outlined in Figure 1.6. The long and extensive route that must occur to acquire these targets can attest to their scarcity in nature. In fact, a previous extraction from the same plant, *Palhinhaea cernua L.* acquired the structure lycopalhine A,[41] along with the precursor obscurinine, which diverges from the biosynthesis from fawcettimine (Figure 1.6). Undoubtedly, there must be environmental and genetic differences that affect the plant's chemotype, but until they are better understood or can be controlled, synthetic methods are the best option for targeting these molecules.

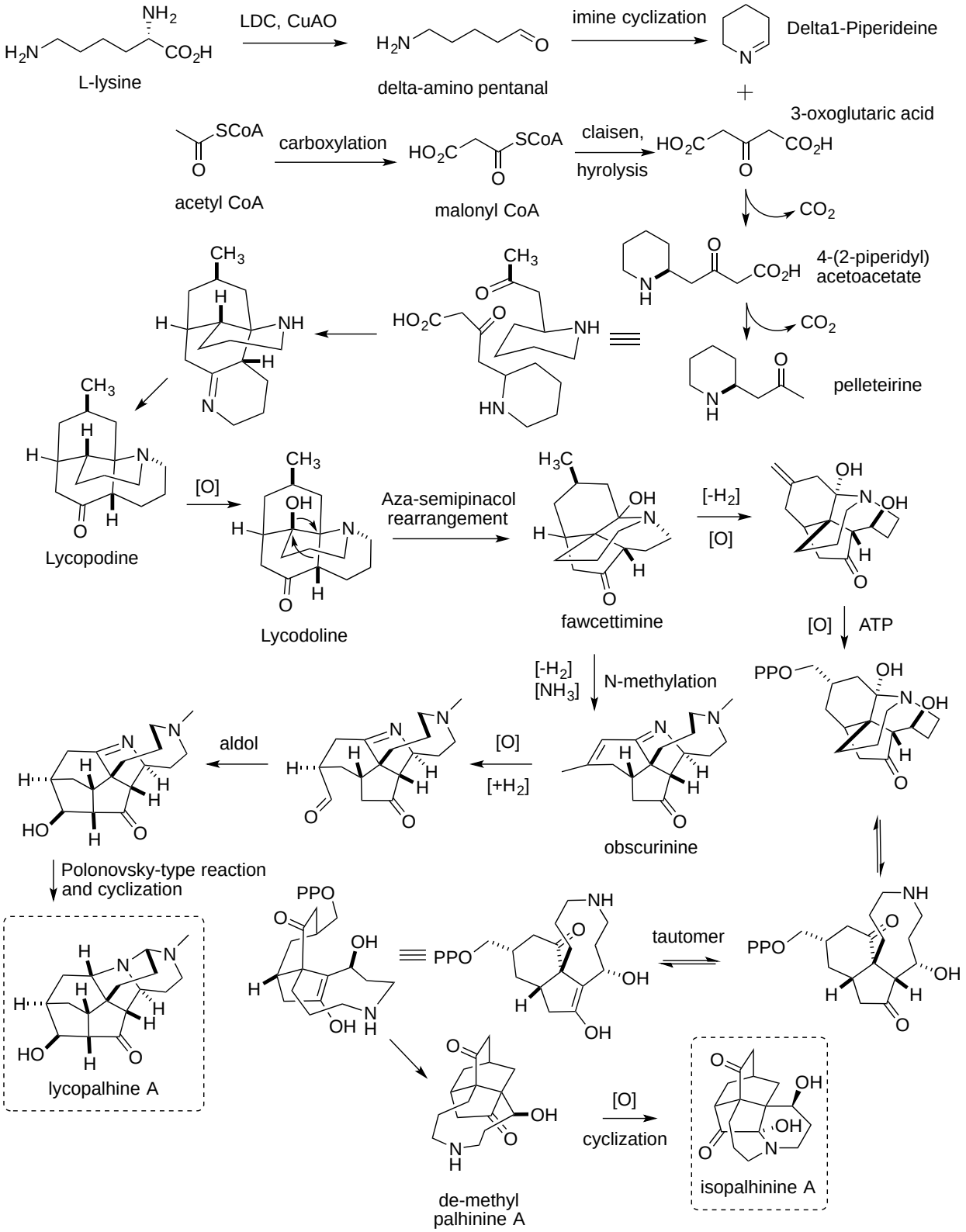



Figure 1.6 Full biosynthetic pathway of isopalhinine A and lycopalhine A, chemical constituents of *Palhinhaea cernua* L., beginning with lysine and acetyl CoA.

*Future Directions*

The Schindler lab's discovery of an increasingly active gibberellin scaffold set the stage for the types of natural product targets of interest. Accordingly, our areas of method development stem from the structural features uniquely common to these molecules. A quaternary reductive aldol reaction has the potential to construct some palhinine alkaloids. Developing this Lewis base-catalyzed reaction was the primary goal of this dissertation, and it was also examined computationally and could be used towards the isopalhinine core.

Parts of this chapter could be included in an introduction when we publish the synthesis towards/of isopalhinine A. Other parts could be included in an introduction for a secondary reductive aldol paper, or a mini-review of method development.

## CHAPTER II: Total synthesis towards isopalhinine A

*Abstract*

We aim for a total synthesis of isopalhinine A, more generally, the palhinine core. Structure-assembling and stereochemistry-building steps for this synthesis sequence include a Birch reduction, Diels Alder, and Lewis base-catalyzed quaternary reductive aldol. To compare strategies, previous syntheses towards the palhinine *Lycopodum* alkaloids are described, specifically the recent synthesis of palhinine A by Fan. Our retrosynthetic strategy for the target, isopalhinine A, is built around a key reductive aldol reaction from a diterpenoid core and protected amine-containing aldehyde. The bicyclic core was synthesized by a Diels Alder reaction between a Birch reduction lactone diene with methyl acrylate as dienophile. An electron-rich Lewis base catalyzed the reductive aldol with $HSiCl_3$, introducing a quaternary carbon, secondary alcohol, and protected amine into the scaffold. Following the reductive aldol, hydrogenation and isomerization furnished an α-quaternary valerolactam, the synthetic precursor to the unique cyclic hemiaminal of isopalhinine A. From this intermediate, further steps will include a directed oxidation and C-C coupling, which have both been tested on model substrates. Additionally, a chain elongation may be utilized because of substrate bias for the 6-membered lactone for the Birch reduction and reductive aldol steps. The 7-membered lactone underwent differing isomerization patterns following the Birch reduction, and these side products and enolate intermediates were lower in energy by DFT. Although Birch reduction isomerization proceeded as required with an open-chain system, the reductive aldol reaction was significantly impaired with this corresponding open-chain substrate.

*Target structures and background*

The clubmoss *Palhinhaea cernua* is used for treating inflammation in herbal medicine.[42] To provide experimental evidence for this phenomenon, rats were miserably exposed to inhaled silica to irritate their lungs, and it was found that an injection of the *Palhinhaea cernua* herbal medicine Shen Jin Cao, either as a preventative or post-exposure therapy, could decrease the

severity of lung cellular irritation after dissection.[43] Since these natural product extracts are a complex mixture,[44] the identity of the therapeutic molecules is unknown.

Still today, new isolated structures continue to be found from this clubmoss, and it is just one of many species with its own unique and variable collection of chemical constituents. Synthesis of these alkaloids and other chemical species would be a helpful tool for elucidating which components are responsible for the observed biological effects. Furthermore, these unique scaffolds are worth synthesizing to expand chemical space for drug discovery. Because their congested core structures distantly resemble known diterpene NF- κB inhibitors, the palhinine alkaloids are an intriguing and worthy synthesis target (Chapter I).

Although most commonly found in Asia, nodding clubmoss is also found in the southern Atlantic US and Gulf of Mexico.[45] Lycopodium powder is used in cosmetics because of its anti-moisture properties.[46] This powder, made of dried spores, is also as a unique explosive dust called Dragon's Breath that has suitable properties for pyrotechnic entertainment.[47] Since this plant has multiple commercial uses, in addition to medicine, synthesis can be endorsed as a conservation effort. If its active components can be synthesized, harvesting the species could become less necessary for medicinal purposes.

Some isolated palhinine natural products have produced only negative results against all assays thus far. Isolated isopalhinine A and palhinines A-C were found to be ineffective against acetylcholinesterase (AChE) and butyrylcholinesterase (BChE), targets for treating neurogenerative dieaeases such as Parkinson's and Alzheimers.[48] Due to the limited amount of palhinines B & C, only isopalhinine A and palhinine A could be evaluated for cytotoxicity against chronic myelogenous leukemia (K562), promyelocytic leukemia (HL-60), liver cancer (SMMC-7721), lung cancer (A-549), breast cancer (MCF-7), and colon cancer (SW-480) human tumor cell lines, but no cytotoxicity was observed. They did not display antifungal activity against *Candida albicans*.

Nevertheless, their cage-like core structure bears structural resemblance to known NF-κB inhibitors, the gibberellins, so even if the natural products themselves may not be reactive molecules, their scaffolds could be modified to add more electrophilic sites to mimic such functional molecules. An efficient route to these alkaloids will allow us to synthesize structures and analogues for NF-κB inhibition studies. At the chemistry stage of this project, constructing efficient methods towards these scaffolds, as well as the structurally similar but distinct bicyclic

*ent*-atiserene diterpenes, is the primary goal. No successful synthetic strategy to isopalhinine A has been reported yet since its isolation in 2013, though palhinine A has been made recently (2017) by the Fan lab (Figure 2.1). There have been many attempts and different strategies since the structure of palhinine A was elucidated in 2010.

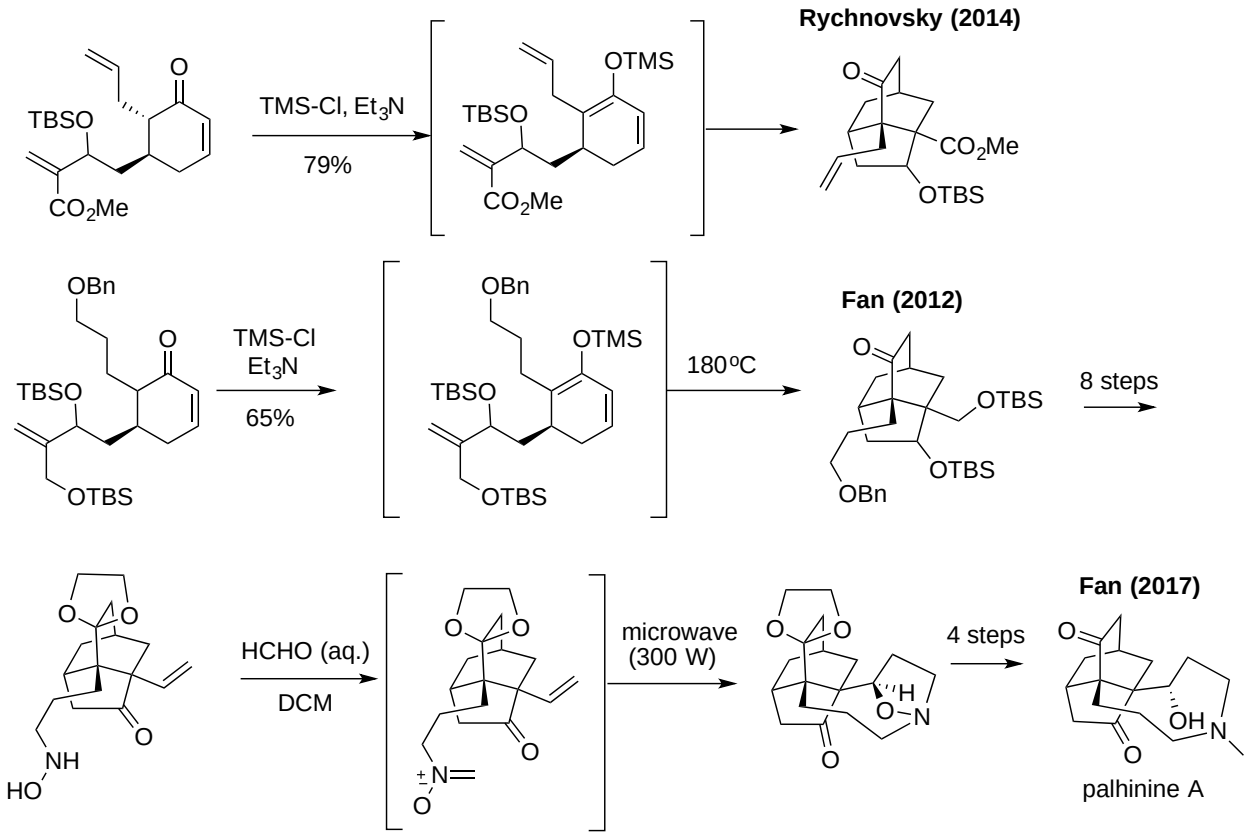



Figure 2.1 Strategies for accessing the palhinine core using a TMS-enolate intramolecular Diels Alder reaction by Fan and Rychnovsky. Elaboration of this core by Fan generated palhinine A in 2017.

*Synthesis of palhinine A by Fan*

The Fan group constructed a bicyclic core in 2012 by an intramolecular Diels Alder reaction with a TMS-enolate and a pendant disubstituted alkene,[49] (Figure 2.1). Five years later in 2017, in eight steps they could prepare palhinines A and D from this intermediate.[50] From the tricyclic ketone triol, they synthesized a substrate for the key azonane ring-building 1,3-dipolar cycloaddition. The further reactions of N-methylation, reductive cleavage, and alcohol inversion then furnished the target palhinine A. They were able to synthesize 15.4 mg, but did not mention biological studies.

The Rychnovsky lab reported a similar strategy to the palhinine core, using a Morita-Baylis-Hillman reaction to append the dienophile fragment for the intramolecular Diels Alder reaction.[51] (Figure 2.1)

*Towards the palhinine core*

As shown by Fan and Rychnovsky, an intramolecular Diels Alder reaction is effective for generating this three-dimensional core. These strategic reactions also introduce a cyclopentane ring beneath the bicycle because the dienophile is linked to the ring by two methylene units. Splendidly, the bridgehead carbonyl is formed as well from the TMS-protected enolate. To produce the diene, the thermodynamic enolate was formed from a 4,5-dialkyl substituted cyclohexenone. This enolate-alkene then underwent an intramolecular Diels Alder reaction with the pendant alkene arm, forming a tricyclic scaffold from one ring.

Additionally, other strategies use aromatic rings as precursors for dienes. The group of Xuegong She has reported two associated construction strategies (Figure 2.2). They used the oxidant $PhI(OCOCF_3)_2$ to de-aromatize a methoxy- and alkyl tosyl amine- substituted phenol. Exogenous hydroxymethacrylate was introduced to nuclophilically attack the activated electrophilic ring at the methoxy position. This serves as the attached dienophile for the [4+2] cycloaddition,[52] forming a tricyclic keto acetal. The ester on this intermediate was chain-elongated and converted to an alkyl bromide in four steps, followed by intermolecular 5-exo-trig radical cyclization to generate the southern 5-membered ring.

The team reported that they currently could not synthesize the 9-membered azonane ring from this intermediate. Their new additional approach uses a larger, synthetically accessible 12-membered ring to be later constricted into the smaller and more strained 9-membered ring. They applied the same oxidative de-aromatization strategy, however with an appended alcohol rather than exogenous hydroxymethacrylate, to generate a 12-membered macrocycle.[53] Oxidation of the non-nucleophilic alcohol with DMP activated the substrate for an intramolecular Diels Alder reaction, constructing a 9-membered ring tetracyclic core (Figure 2.2).

Further methods for bicyclic ketone cores include a bimolecular domino Michael reaction, as demonstrated by Maier in 2013 (Figure 2.3).[54] The alkyl-OTBDPS cyclohexenone was kinetically deprotonated with LiHMDS, and then methyl acrylate was added. Enolate conjugate attack of methyl acrylate forms a new enolate, which adds to the Michael acceptor of the original cyclohexanone. This forages a tricyclic ketone with neighboring ester and quaternary

alkyl –OTBDPS functionalities. Subsequent steps convert the methyl ester to its corresponding chain-elongated aldehyde, which is used for an intramolecular aldol reaction to create the cyclopentanone ring.

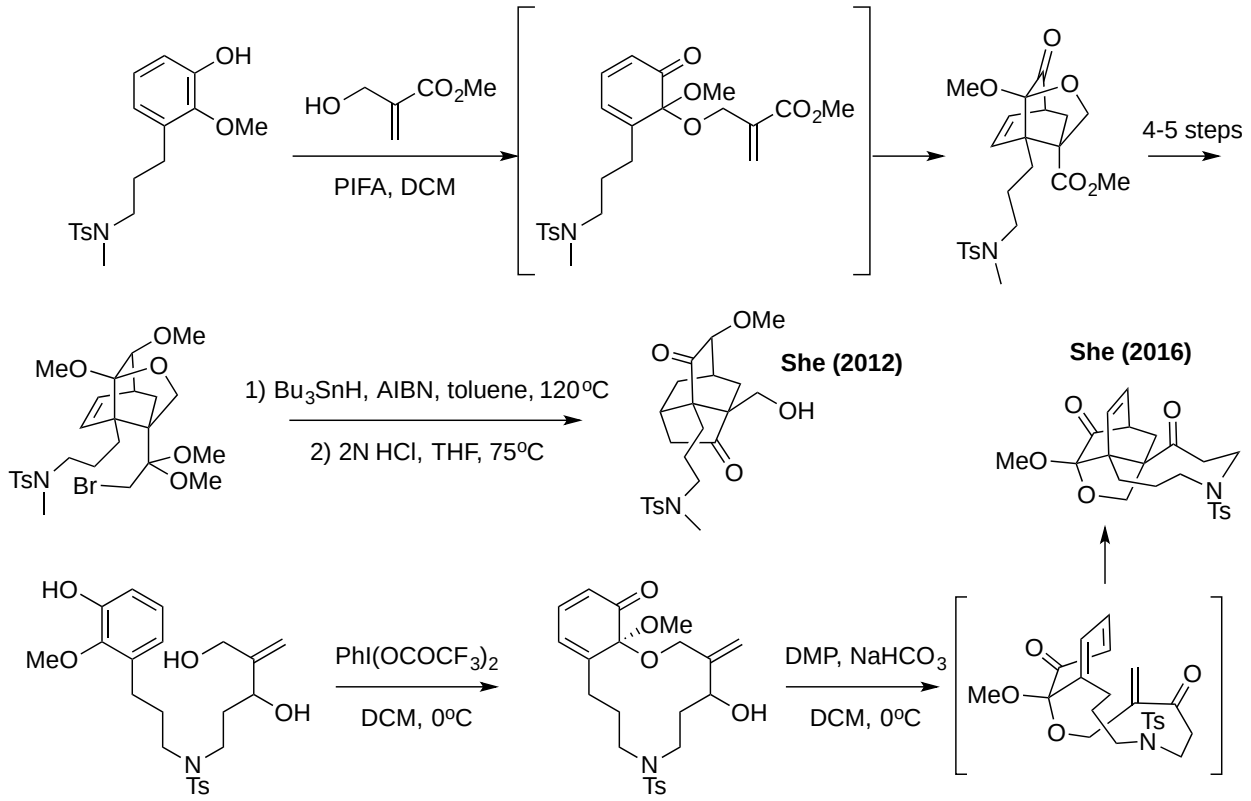



Figure 2.2 Two oxidative de-aromatization approaches toward the skeleton of palhinine A by Xuegong She and coworkers.

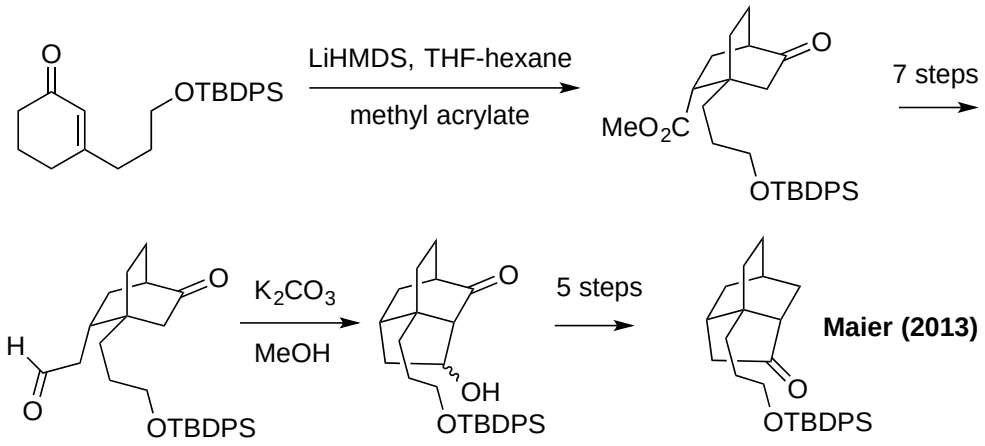



Figure 2.3 Maier (2013): A bimolecular domino Michael reaction to construct the bicyclo[2.2.2]octane motif, as well as an intramolecular aldol to create the southern 5-membered ring.

*Intermolecular Diels Alder and Reductive Aldol Approach*

Because the lab is coming from the perspective of synthesizing bicyclic *ent*-atiserene diterpenoids, not just the palhinine alkaloids as our only target, our strategy is new and uncommon in its approach. We employ a simple intermolecular Diels Alder reaction that generates a building block that could potentially be used for the divergent syntheses of many 1,2,6-trialkylbicyclo[2.2.2]octane natural products (Figure 2.4, bottom). The building block synthesis is described in this chapter, along with how this intermediate was elaborated into a structure that can be used towards isopalhinine A (Figure 2.4, top).

Our palhinine synthesis strategy relies on the success of a key reductive aldol reaction that generates a quaternary carbon between a secondary alcohol and carbonyl. Since many natural products, not just the palhinines, contain this motif, there was reason to develop a general method. Although reductive aldol reactions are not new, the majority of these methods were built and optimized around simpler substrates. Further, ketones have been more common substrates than esters and amides because of their reactivity. Our substrates required a controlled system so that the aldehyde is not reduced to the alcohol, but is rather activated for being attacked by the enolate. Viable Michael acceptor (reduction) and aldehyde (aldol) substrates for this method with an electron-rich aromatic Lewis base catalyst and $HSiCl_3$ are discussed in Chapter III. Lewis bases and substrates were evaluated for individual reaction steps computationally, which is discussed in Chapter IV.

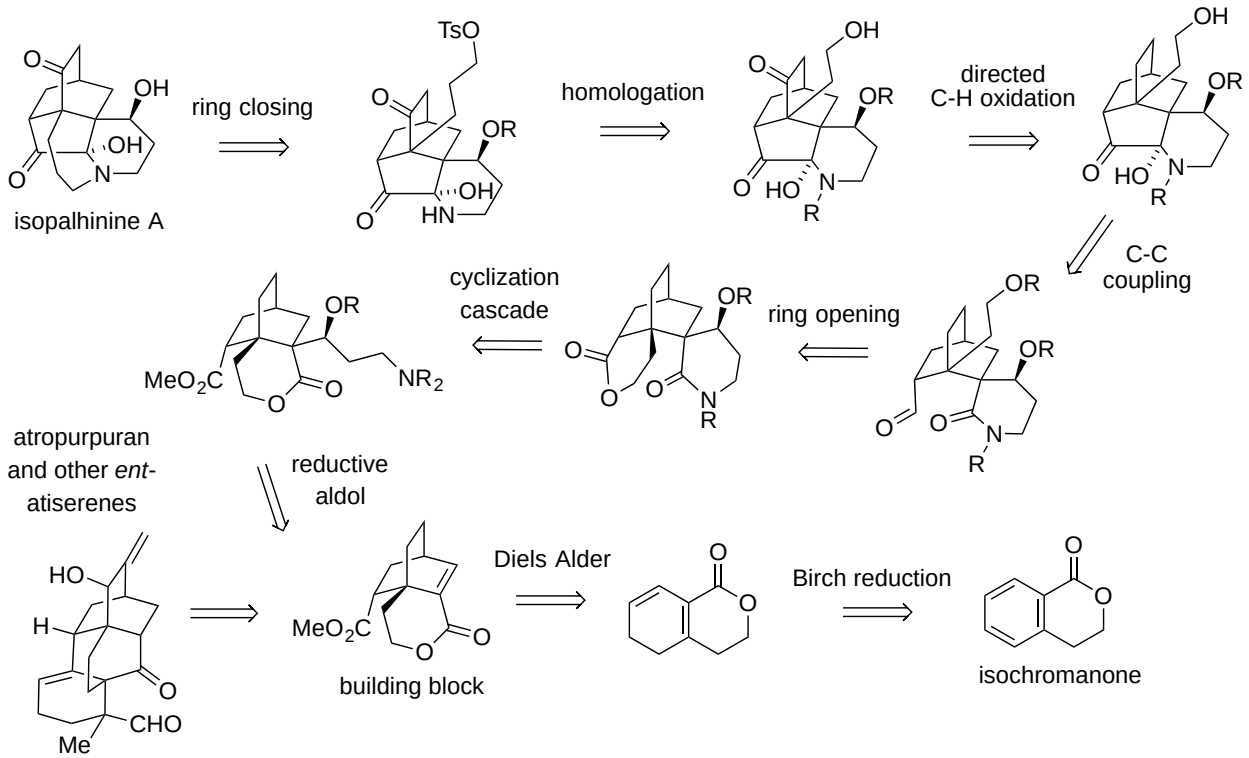



Figure 2.4 Retrosynthetic analysis of isopalhinine A. The key building block is a substrate for a reductive aldol, and additionally a precursor for diterpenoids.

*Retrosynthesis of isopalhinine A*

From a retrosynthetic perspective, the molecule can be broken apart ring by ring. Since azonane is found in the palhinines, but not isopalhinine, the difficult construction of a 9-membered ring can be avoided. To circumvent the effort in making a strained ring, the final ring-closing step of the synthesis will instead be construction of a 7-membred ring (Figure 2.4). Prior to this final ring closure, an additional carbon is needed from the starting material because the key reductive aldol reaction works successfully with 6-membered ring lactones. Unless the reductive aldol and Birch reduction reactions can be modified to accommodate substrates more generally, a chain homologation will be necessary.[55]

Isopalhinine A contains a bridgehead carbonyl, which will be installed by directed oxidation methods, for example by using the Fe(PDP) catalyst developed by the White group (Figure 2.5a).[56] The alcohol functional group, or its carboxylic acid derivative, originally tied up in the lactone ring, will be used as the directing group after opening the lactone. C-C coupling can generate the cyclopentane ring, and we have demonstrated this on a simpler substrate (Figure 2.5b).[57]

For this model system, global reduction of the Diels Alder product afforded a symmetric triple alcohol. The least hindered, central primary alcohol could be selectively protected with a bulky TBDPS protecting group, and then the two flanking primary alcohol groups were oxidized to aldehydes. After C-C coupling, double oxidation, and alcohol de-protection, we found that a hemiacetal was spontaneously formed from the reactive 1,2-diketocyclopentane and de-protected alcohol. In the isopalhinine system, a ketone neighboring a hemiaminal may not be as strongly electrophilic as a 1,2-diketone. If a similar issue is encountered, the newly formed 1,2-diol may need to be protected rather than oxidized so that the directing group is not abstracted by a strong nearby electrophile.

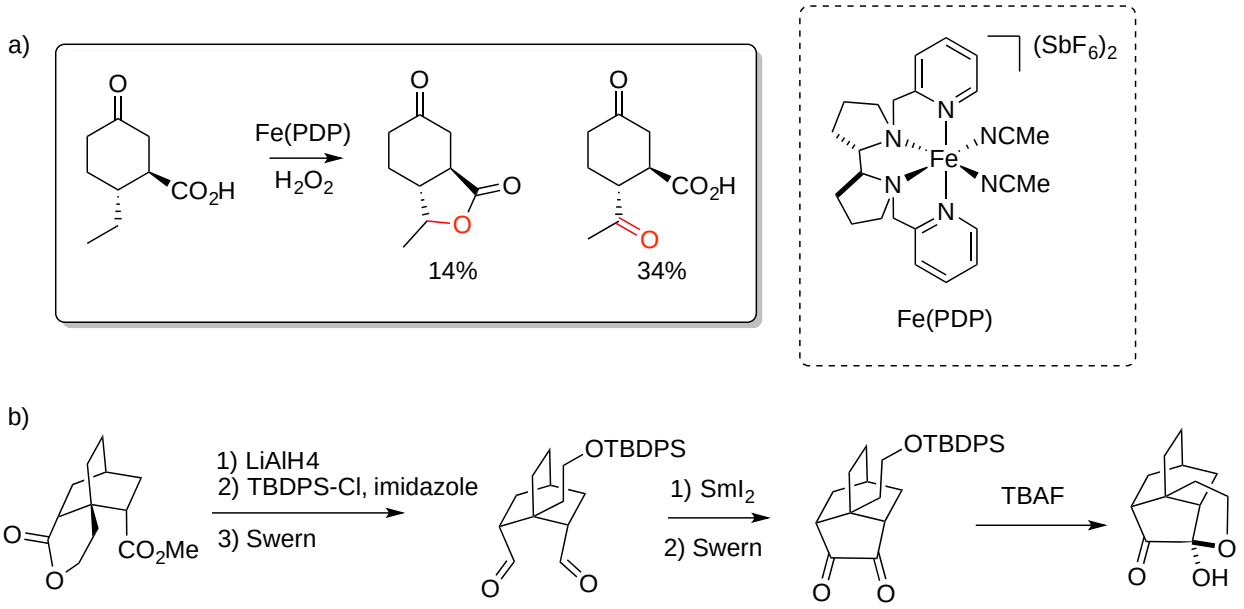



Figure 2.5 a) Literature precedent for a carboxylic acid-directed oxidation by the White group. b) Samarium iodide coupling on a simplified model substrate (without the reductive aldol fragment of the molecule).

Before the directed oxidation step, the directing group is part of a lactone ring. Hydrolysis or reductive cleavage of the lactone will free the alcohol so that it can be used as a directing group. Taking advantage of the relative stability of lactams over lactones, this densely functionalized core can be constructed by an N-deprotection, lactam-forming, lactone-opening cascade from the N-protected reductive aldol product (Figure 2.4). The simple building block substrate, formed by an intermolecular Diels Alder reaction with methyl acrylate, contains a strained and highly electrophilic Michael acceptor. It is an ideal substrate for the reductive aldol reaction, as it permits a select position to reductively form an enolate for an aldol reaction in the

presence of other, enolizable functional groups such the other ester. The diene is formed from a Birch reduction and enolate isomerization on commercially available isochromanone. (Figures 2.4, 2.6a)

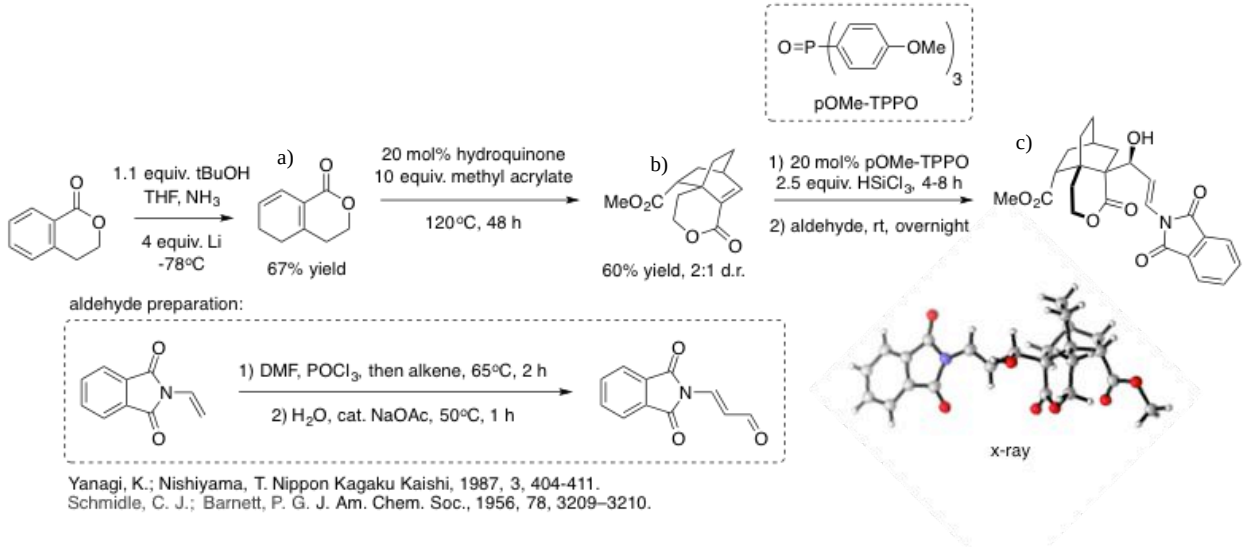



Figure 2.6 Beginning forward synthesis toward the palhinines. These first steps include a) Birch reduction directly on isochromanone, b) Diels Alder with methyl acrylate, and c) reductive aldol.

*Birch Reduction on Isochromanone*

Describing the synthesis in the forward direction, we begin with the lactone isochromanone. Although it is commercially accessible, its relatively high cost and limited available quantity ($63.40/g, 5g from TCI America) drove us to synthesize it instead. Isochroman ($2.38/g, 50g from Alfa Aesar) was purchased and oxidized with a mixture of $KMnO_4$ and $MnO_2$.[58] Initially, Birch reductions[59] on isochromanone were unsuccessful, generating a mixture of starting material and degradation. Both sodium and lithium were tried as sources of solvated electrons, as well as the addition of methanol as a proton source. With these conditions, we could not generate any of the dearomatized products. We hypothesized that the lactone ring was reduced instead of the aromatic ring.

To eliminate the issues associated with the inherent sensitivity and electrophilicity of lactones, we instead employed a more robust strategy that had been reported on the 5-membered ring analog, phthalide.[60] This three-step process involved 1) basic lactone hydrolysis to the ring-opened system: primary alcohol and sodium carboxylate salt, followed by complete removal of water using a lyophilizer, 2) Birch reduction, and 3) lactone re-formation using coupling reagents DCC or EDC-HCl. This process, although scalable for up to 20g batches, was time consuming

due to the requirement to completely remove water following the hydrolysis before the Birch reduction. For large batches, water removal could require several days with repeated suspension and freezing to remove all water to form a solid powder or foam for the Birch reduction.

We investigated a one-step procedure that was tolerant of esters. We found a Birch reductive alkylation procedure that used *tert*-BuOH as the proton source and THF as a co-solvent.[61] The excessive need for THF to properly dissolve the substrate limited this procedure to 8g of isochromanone batches in a 2L flask. Although less amenable to scale, this one-step procedure could be accomplished in one day, allowing more rapid access to the diene. (Figure 2.6a) Likewise, this procedure fully isomerized the product to the preferred conjugated diene. Under basic conditions, the enolate is formed, and when quenched during the acidic aqueous work-up, the formation of the anticipated diene is favored. (Figure 2.7a,b)

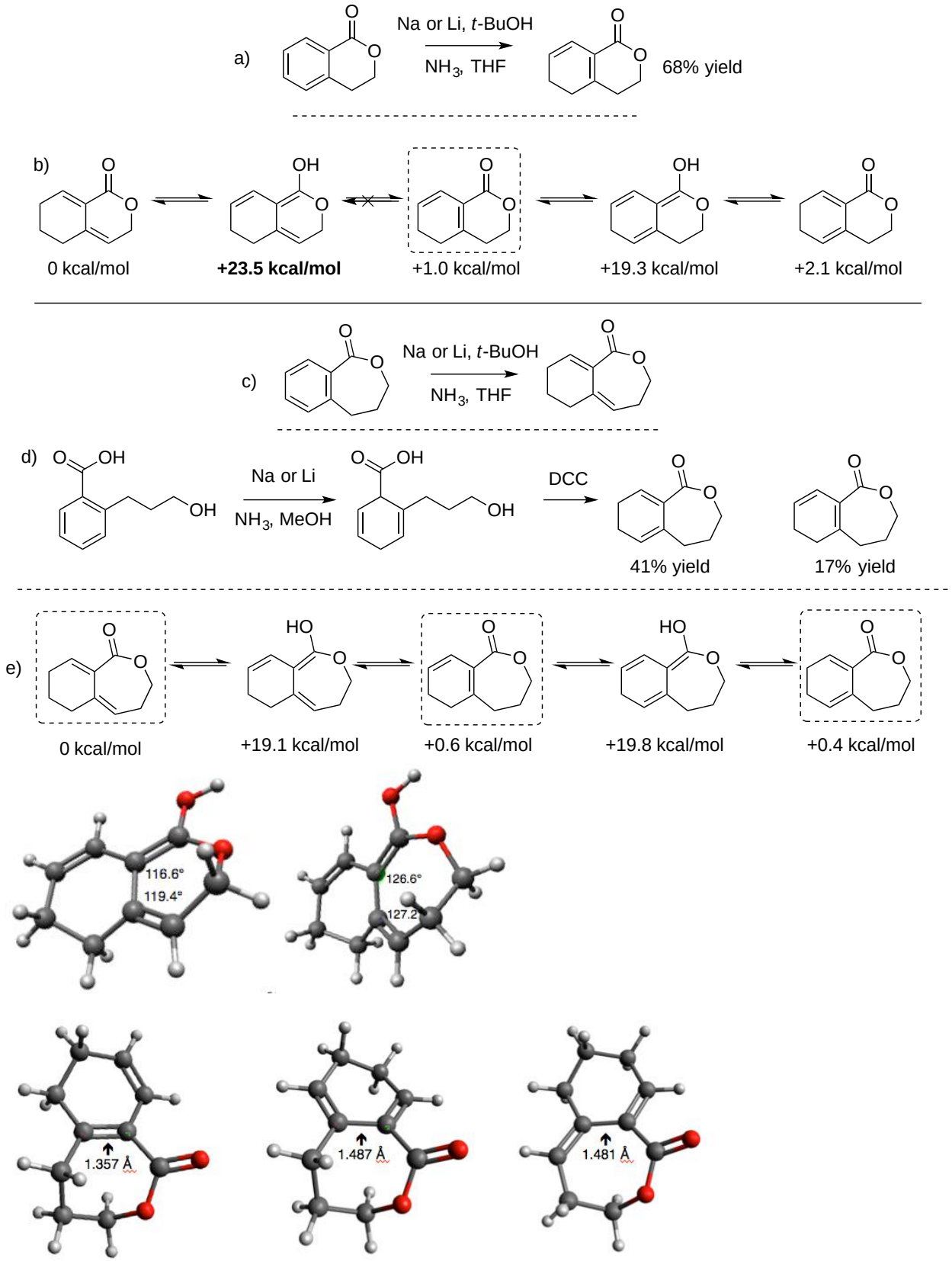



Figure 2.7 DFT calculations for lactone diene alkene isomers from a Birch reduction.

*Intermolecular Diels Alder with Methyl Acrylate*

Following the Birch reduction on isochromanone, the diene was subjected to a Diels Alder [4+2] cycloaddition reaction with methyl acrylate as the dienophile. Considering that both the diene and the dienophile contain electron-withdrawing ester groups, this Diels Alder reaction does not exclusively fit into a single category of normal or reverse electron demand. Having electron-withdrawing groups on both partners, rather than just one, widens the HOMO-LUMO energy level gap. This is why the reaction must be heated. Similar reactions have been reported with carboxylic acid-substituted aryl groups, which is electronically similar to this aromatic lactone.[62] (Figure 2.8) Because of the secondary orbital overlapping interactions with the diene and the ester of methyl acrylate, the endo products are formed selectively, positioning the ester downwards. This matches fortuitously with the structure of the palhinines.

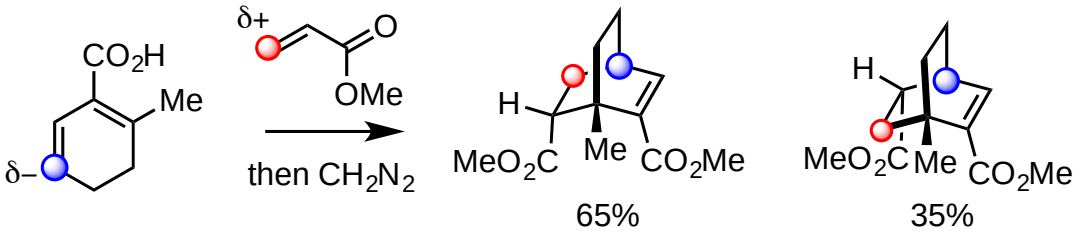



Figure 2.8 Literature example of an intermolecular Diels Alder reaction with electron-withdrawing groups on both the diene and dienophile.

In this example (Figure 2.8), the major product is a consequence of electronic matching of the two substrates. However, steric interactions between the ester, methyl, and carboxylic acid groups play a role as well. The major, more crowded regioisomer is formed in 65% yield, and the minor, less crowded but electronically mismatched regioisomer is formed in 35% yield.

The reaction of our diene lactone with methyl acrylate most closely resembles the example in Figure 2.8. Indeed, our reaction produces a mixture of regio-isomeric products in the same 2:1 ratio. (Figure 2.6) Ahlam Armaly discovered that the major regioisomer was insoluble in the solvent diethyl ether, while the minor product was soluble. This characteristic property allowed us to obtain pure material straightforwardly. With a crude Hexanes/Ethyl Acetate silica flash column, to remove excess methyl acrylate, hydroquinone, and polymer, the mixture of regioisomers co-elutes, but after collection is rinsed with diethyl ether to dissolve the other regioisomer, precipitating and collecting the preferred product by filtration (Figure 2.6b).

*Chain-elongated route*

After success with isochromanone for the Birch reduction and Diels Alder sequence, we wanted to extend the substrate scope to the chain-elongated 7-membred-ring lactone, considering that our final target, isopalhinine A, has this additional methylene. Unfortunately, for the Birch reduction, this system did not react in the same way as anticipated. For the 6-membered ring lactone, the diene fully isomerizes to the desired di- and tetra-substituted alkene, both when the Birch reduction is done on the open system or directly on the lactone (Figure 2.7a). For the 7-membered ring, different alkene isomers were favored. The desired alkene could be obtained as a minor product using the open-chain strategy, and moreover the substrate synthesis was demanding compared to isochromanone (Figure 2.9).

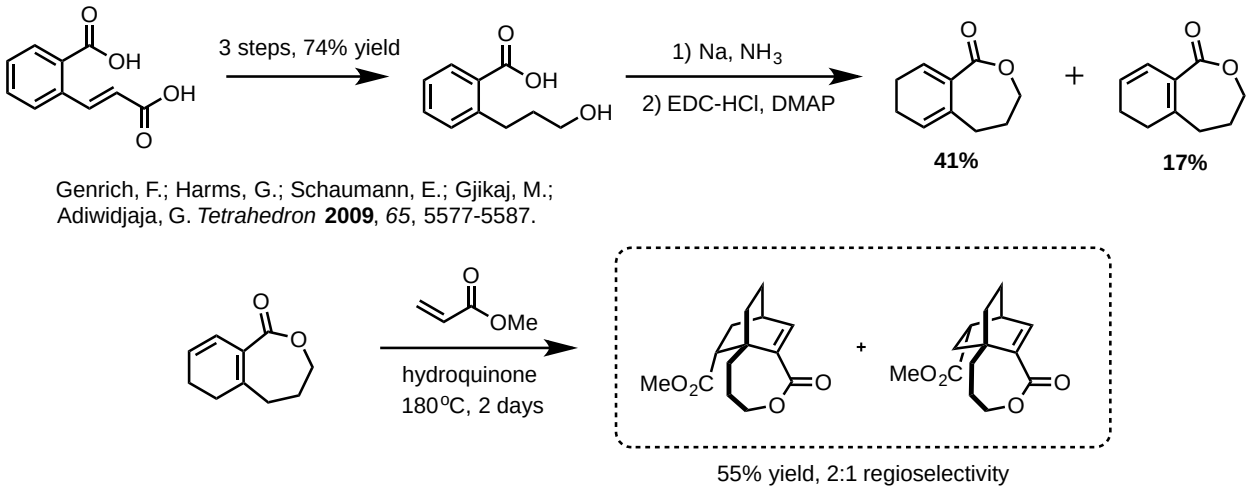



Figure 2.9 Chain-elongated synthesis. The preferred product, although minor, could be isolated and subjected to [4+2] with methyl acrylate.

Our first attempt Birch reduction was done on the open acid and primary alcohol (Figure 2.7d). But after ring closure, the di- and tetra-substituted product was only a minor component, formed in 17% yield with EDC-HCl to form the 7-membered lactone. The major product was, instead, a different alkene isomer, doubly tri-substituted, which we calculated to be more thermodynamically stable for the 7-membered ring because it has a single, longer rotatable bond at the connecting position can alleviate ring strain (Figure 2.7e). This isomer is unfortunately not a valuable intermediate towards our target structure. We could observe the same effect with bulky ester substrates (Figure 2.10). In this case, steric hindrance can explain the preference for a single bond, so that the neighboring groups can have more space.

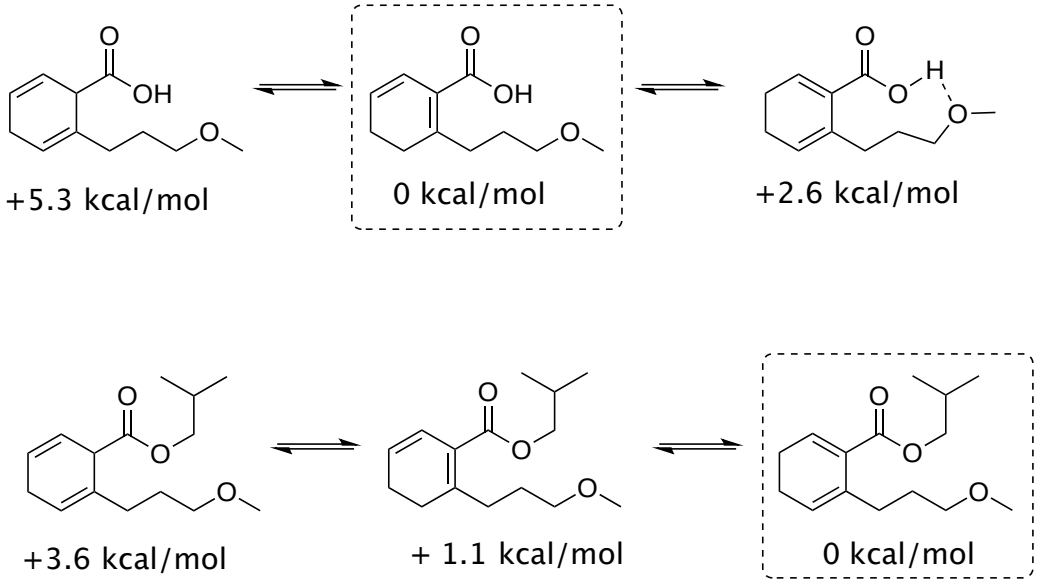



Figure 2.10 Observed and calculated differences in isomerization following the Birch reduction on acyclic carboxylic acids & esters. Besides a strained 7-membered ring, an increase in steric bulk can also favor the unexpected alkene isomer.

After developing the lactone-direct procedure and subjecting the 7-membered ring to these conditions, we isolated another different undesired alkene isomer, which we propose results from deprotonation of the lactone ring (enol intermediate of +19.1 kcal/mol in Figure 2.7c), but is not formed with the 6-membered ring due to the higher enolate barrier of +23.5 kcal/mol (Figure 2.7b). The larger ring size allows more flexibility. Even though both substrates theoretically have the same lowest energy isomer, only the 7-membered ring's enolate is low enough in energy to allow access.

Getting back to the synthesis, the desired diene could be made as a proof of concept, albeit in low yield and higher step count (Figure 2.7d). We were able to isolate this after EDC coupling and subject it to a Diels Alder reaction with methyl acrylate, producing the same 2:1 ratio of products in a 55% yield (Figure 2.9). Additionally, washing with $Et_2O$ could purify this product.

This product was a poorer substrate for the reductive aldol step in comparison to the 6-membered ring (Figure 2.11). This observation may not necessarily be true, though. We did have much less material to work with and the reaction was not easily reproducible. Preliminary calculations (Chapter IV) suggest that the substrate should actually be very similar to the 6-membered ring in terms of reduction transition state energy. Nevertheless, we decided to

currently pursue the 6-membered ring substrate for the total synthesis, as it would allow a larger scale and more material available for later steps.

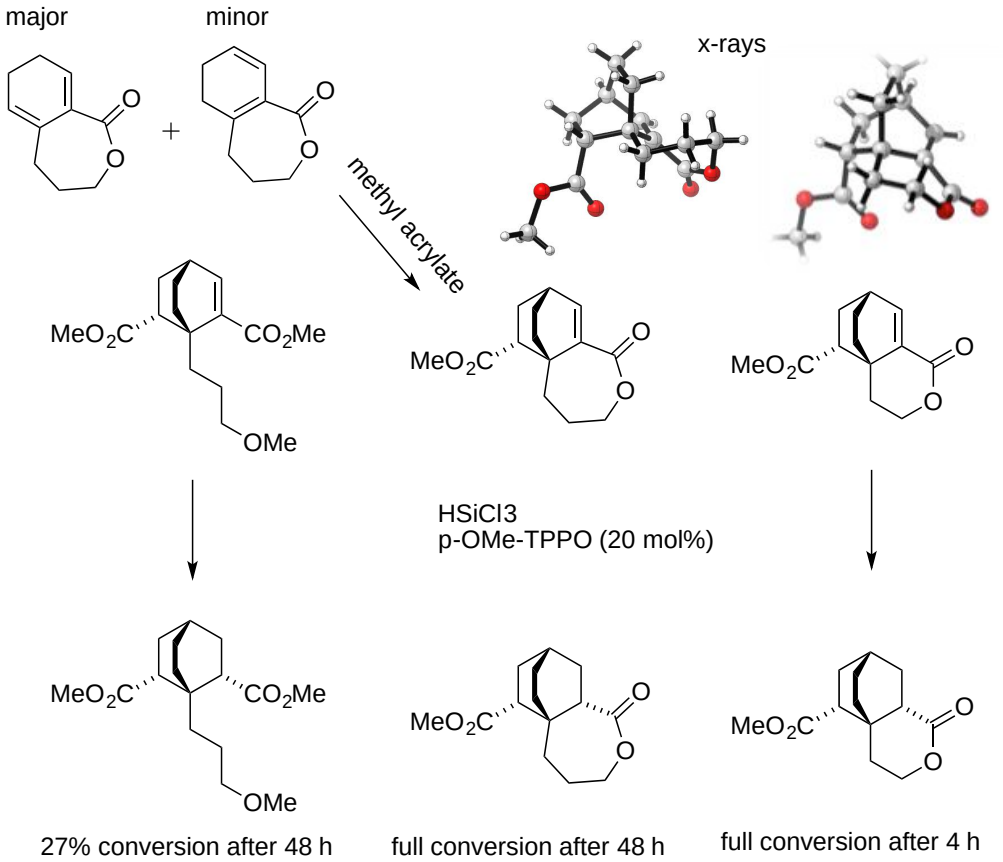



Figure 2.11 Relative reduction rates of isopalhinine Michael acceptors: 6-membered lactone > 7-membered lactone > open ester.

*Lewis Base Reductive Aldol*

The next step, the reductive aldol, combines this Michael acceptor lactone core with a cinnamaldehyde analog containing phthalimide to generate a quaternary carbon neighboring a secondary allylic alcohol, diastereoselectively (Figure 2.6, 2.12, 2.13). This reaction was established from a procedure reported by Nakajima, which was primarily used for disubstituted alkene substrates.[63] The development and substrate scope of this reaction is discussed in Chapter III. A new electron-rich phosphine oxide catalyst was used specifically to make these quaternary products, since the reported method for secondary and tertiary centers was not directly applicable without side products or inefficient conversion.

During preliminary investigations, essentially repeating the identical reaction conditions and catalysts of the original paper on our substrates, we realized the limitations of these catalysts for quaternary carbons. The only reported example of a quaternary product was achieved in 39% yield with HMPA as the catalyst, and we found a similar result when we used HMPA with our model system lactone, achieving 45% yield. The starting material was fully consumed, and there was 26% yield of a side product (reduced lactone). Using the other prevalent catalyst from that paper, TPPO, gave a similar yield of 43%. Yet, the yield based on recovered starting material was considerably higher (80% yield brsm, 46% recovered starting material).

The low yield with TPPO was due to a slow rate of reaction, not regarding any significant difficulties with the aldol reaction or side product formation. This gave us the opportunity to create a catalyst specific to the demanding requirements of these systems: a catalyst that might react with the same positioning as TPPO, but also one that is strongly Lewis basic enough to fully reduce the starting material, like HMPA. We hypothesized that the aldol reaction was obstructed with HMPA because of the bulk of HMPA's methyl groups nearby the phosphine oxide crowding or breaking up the transition state. To solve these issues of sterics and strength, we placed electron-donating groups at the *para*-postion of the three aryl groups on TPPO, so that the catalyst is increasingly electron-rich, but should remain similar in geometry.

With this catalyst in hand, we could develop a broad method (Chapter III), and in doing so, also explored the tolerance of the aldehyde partner for this reaction. It was found that aldehydes could not contain acidic alpha-hydrogen protons, because the enolate ester would selectively deprotonate the hydrogen and not attack the carbonyl. Because of this, we used a conjugated, cinnamaldehyde derivative containing phthalimide because it had been reportedly made and does not contain acidic protons because of the C=C double bond. However, the C=C double bond also renders the aldehyde a Michael acceptor, so it will undergo the same hydride-reduction chemistry that is intended for the lactone, giving a wide mixture of products (Figure 2.12).

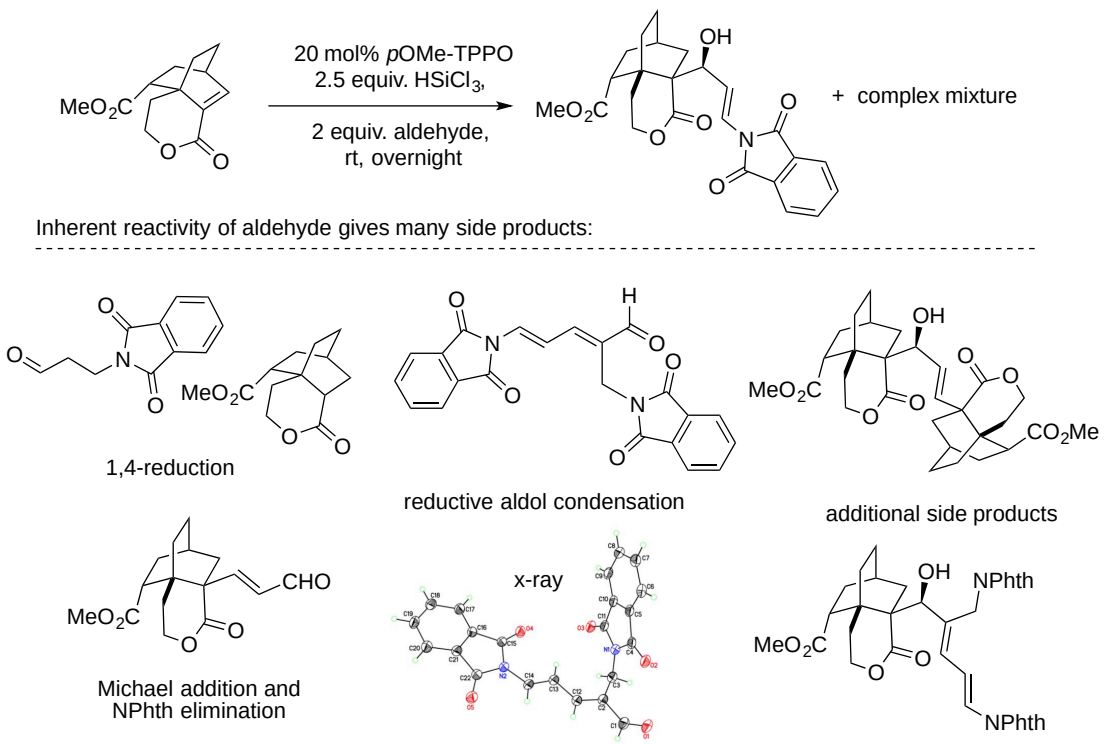



Figure 2.12 Side products encountered when scaling up the reductive aldol reaction towards the palhinines.

Many additional structures are formed because of this chemistry (Figure 2.12). There is also the dual ability of the Michael acceptor aldehyde to be attacked either at the 2-position to generate the aldol product or at the 4-position, which results in elimination of the phthalimide group. Since the reductive aldol product of two phthalimide aldehydes does not create a quaternary center, elimination of water occurs, which creates a conjugated Michael acceptor aldehyde capable of undergoing further reactions. Also, the water released from elimination quenches trichlorosilane and enolate species in the reaction, diminishing reactivity overall.

In an attempt to suppress these side reactions the reaction was cooled to -78°C, but instead, only reduction of the lactone was suppressed, but aldehyde reduction continued to occur. Instead of controlling temperature, we manipulated this reaction by changing the order of addition. Adding the aldehyde hours later, once the lactone enolate has been formed, can reduce the formation of these side products. As a side note to the experimentalist, the desired product, as well as some of the side-products, is quite insoluble in most solvents once precipitated, and it is necessary to sonicate the solid in DCM to re-dissolve the compound completely.

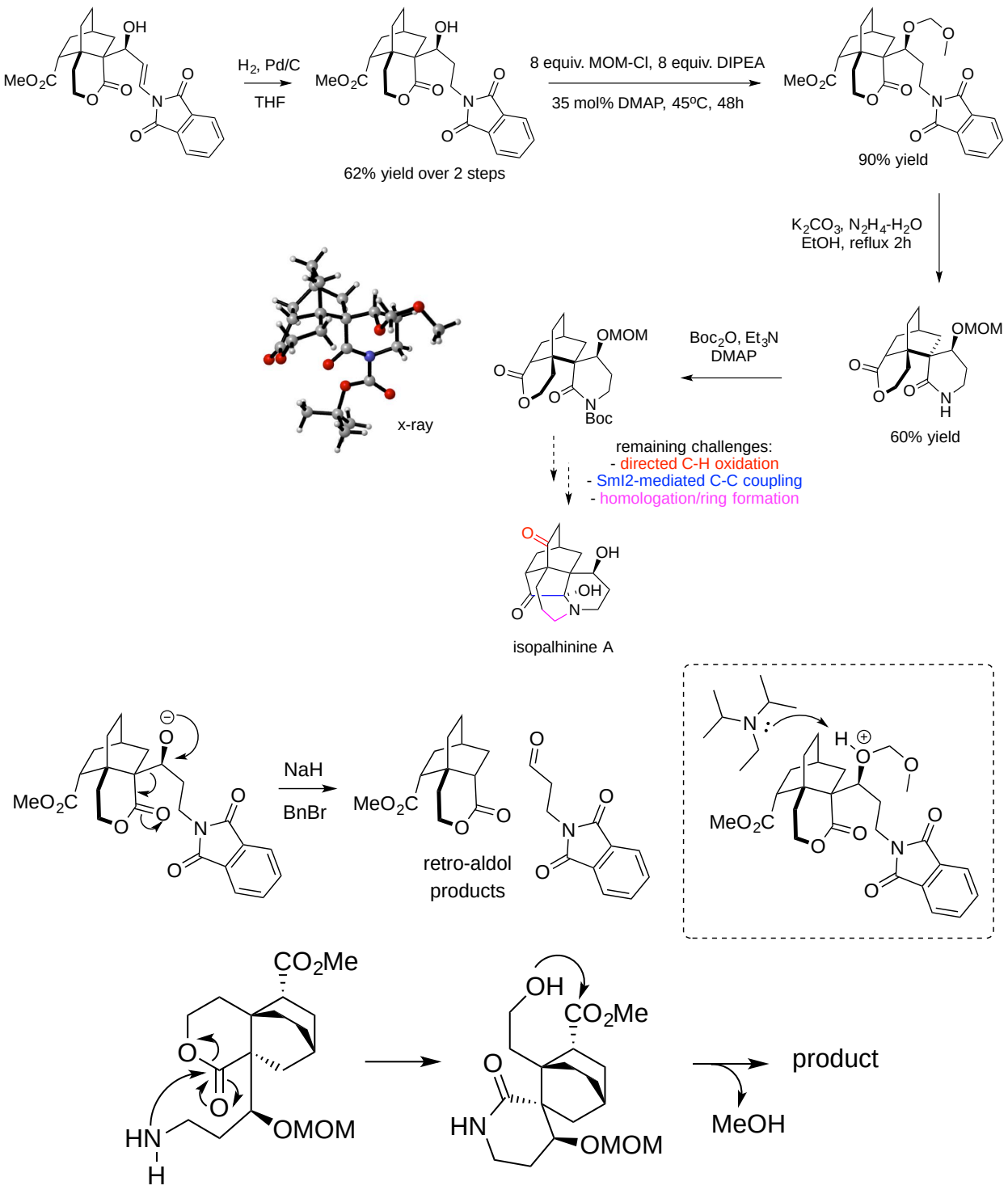



Figure 2.13 Synthesis of the isopalhinine core from the reductive aldol product.

*Hydrogenation, alcohol protection, and isomerization*

Once isolated, the reductive aldol product is then hydrogenated, to remove the double bond that was necessary. (Figure 2.13) This intermediate is soluble in Ethyl Acetate, and is also more stable, less prone to retro-aldol degradation. To further prevent degradation, the alcohol was protected with a MOM group. (Figure 2.13) We attempted to use a more labile protecting group, such as benzyl, but using the strong base NaH resulted in rapid degradation to the retro-aldol products. It is clear that once the alcohol is deprotonated, the substrate will degrade immediately, before the protection takes place. Because of this, we needed a base that was weaker, not strong enough to deprotonate the alcohol outright, but once the alcohol has reacted with an electrophile, a weak base such as DIPEA can deprotonate this positively charged species. This secondary alcohol neighboring a bulky cyclic system is very hindered, so we needed to use a large excess of MOM-Cl and DIPEA, as well as catalytic DMAP. The reaction was heated slightly in a pressure tube and took two days, which is not typical for most MOM protections.

For this route, it is essential to hydrogenate the reductive aldol product prior to MOM-protection. Although MOM-protection of the reductive aldol alkene product directly was apt, and even a bit more efficient than protecting the hydrogenated analog, the problem lies in the hydrogenation of the protected alcohol, which was much slower, and because of this, produced over-reduction side products from phthalimide carbonyl reduction to the amide.

From this MOM-protected and hydrogenated intermediate, we first attempted to reduce the lactone and ester groups to their corresponding lactol and aldehyde groups using DIBAL-H, to prepare the structure for C-C coupling to form the southern cyclopentane ring. However, we observed competing reduction of the phthalimide group, so we endeavored to remove the phthalimide and re-instate a different, less electrophilic protecting group. When we tried to protect the nitrogen as a 2,5-dimethylpyrrole, heating the amine with 2,6-hexanedione and catalytic TsOH, we isolated a distinctive product, where the nitrogen had attacked the nearby lactone ring, which opened up, and the alcohol formed a new lactone ring with the ester, eliminating MeOH. To confirm this structure, we protected the newly formed lactam with a Boc group, and were able to crystallize the product for an x-ray structure. With this lactam, we attempted to form the cyclopentane ring with $SmI_2$; however, this only resulted in cleavage of the Boc protecting group. For this next step, a more robust protecting group is required.

*Future directions*

The main complications of completing the synthesis are the difficulty of gaining material to complete the final steps because the reductive aldol is problematic to scale and purify due to side reactions (Figure 2.12). Finding conditions for a robust reductive aldol is key, and with these in hand, the remaining oxidation and ring formation steps will be elucidated (Figure 2.13). After or prior to completion of the synthesis, electrophilic structural analogs could be synthesized.

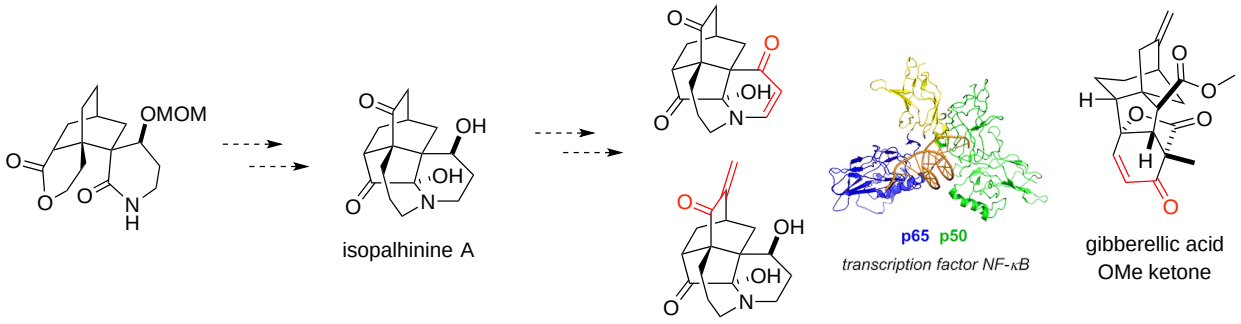



Figure 2.14 Future plans: adding Michael acceptors to isopalhinine.

A collection of intermediates and products from Chapters II and III were submitted to the MScreen Center for Chemical Genomics database at the Life Sciences Institute. The physical samples have not yet been approved to be collected and are located in Chemistry 2632. Contact: Matthew O'Brien and Renju Jacob from CCG when these are ready to submit.

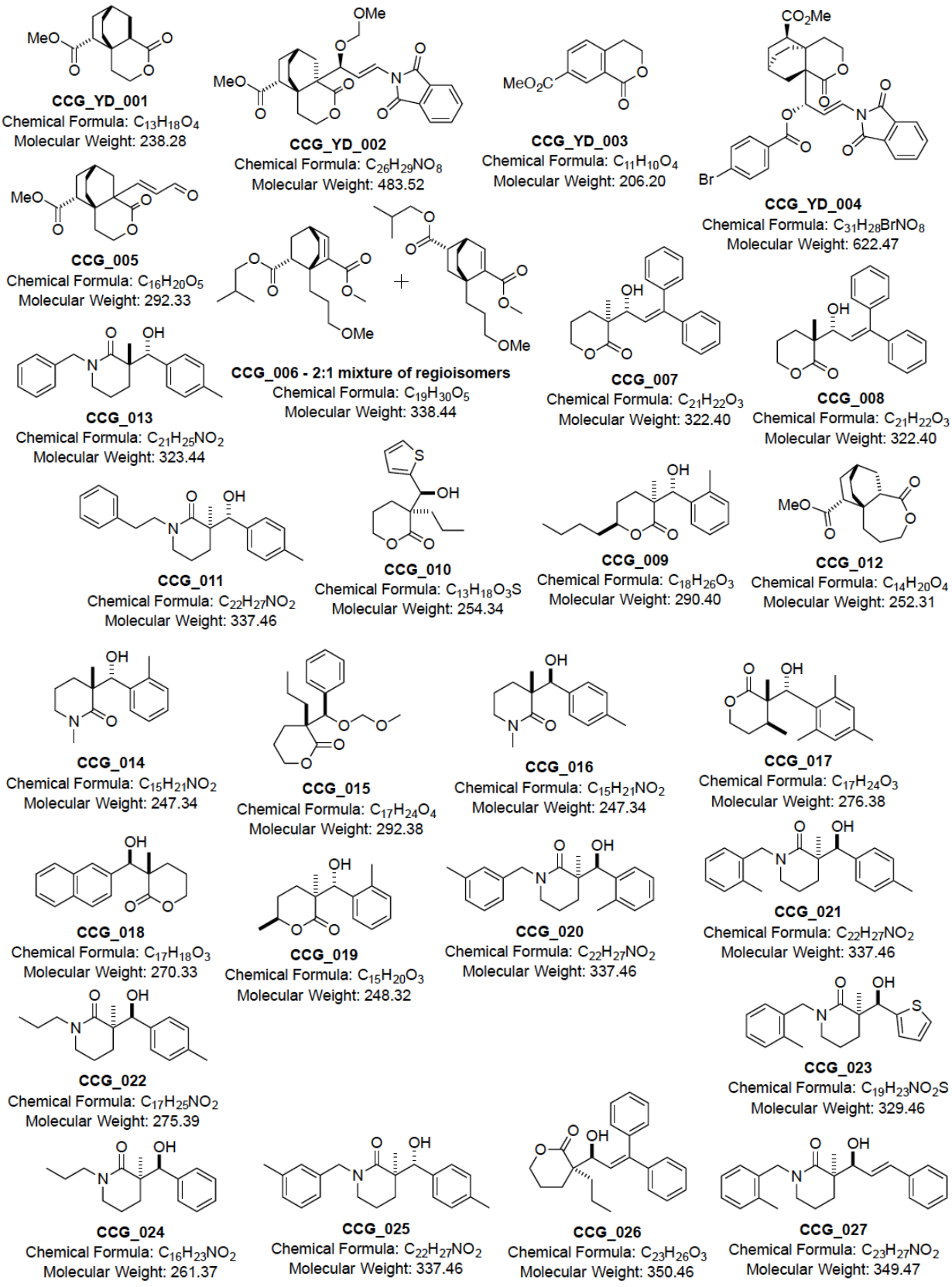



Figure 2.15 Compounds submitted electronically to the Center for Chemical Genomics.

## CHAPTER III: Quaternary Reductive Aldol

*Abstract*

A key step in the synthesis (reductive aldol) required a unique electron-rich Lewis base catalyst specifically for making quaternary products. This section examines different phosphine oxide catalysts and the substrate scope for this general transformation, along with the utility of these quaternary aldol fragments. This approach provides a valuable synthetic alternative for carbon-carbon bond formation in complex molecular settings due to its orthogonal reactivity compared to existing aldol reactions. Based on the method described, lactones, lactams, and morpholine amides bearing quaternary carbon centers are accessible in yields up to 85% and >20:1 d.r.

*Accessing lycopodium alkaloids with quaternary carbons*

The densely functionalized Lycopodium alkaloids have been organic synthesis targets for over 125 years, since Lycopodine was isolated in 1881.[64] More recently, huperizine A from *Huperzia Serrata* has been developed as a symptomatic treatment for Alzheimer's disease, available as a nonprescription dietary supplement in the United States. It works as an AChE inhibitor, resulting in increased levels of the neurotransmitter acetylcholine. In addition to their significant biological activity, this group of molecules is an imperative synthesis target, because the current methods for harvesting huperizine A and other alkaloids are unsustainable and will result in decimation of natural habitats if continued.[65] Typically, these alkaloids can be isolated in only mg quantities from processing kg of plant material. Additionally, the club mosses are known to be slow growing, difficult to cultivate outside of their natural habitat, and inconsistent with regards to their chemical profile.[66]

As a structural comparison, Lycodpoium alkaloids usually contain at least one quaternary carbon (Figure 3.1a, c), and strategies are built around forming this difficult motif. To emphasize the importance and efforts of such methods, Figure 3.1a provides a few examples of how this has

been accomplished to date, as described in the review by Murphy and Sarpong. Williams was able to construct a congested quaternary carbon-containing scaffold by an intermolecular Diels Alder reaction, with which they were able to build a 6-5-9 tricycle and access the targets lycoflexine, fawcettidine, fawcettimine, and lycoposerramine B.[67] Using the same diene as the Williams group, but with a different alkyne-containing dienophile, the Taniguchi group was able to access lycopoclavamine B, lycoposerramine T, and serratine from a slightly more oxidized 6-5-9 tricycle.[68] The Diels Alder strategy, although reliable, is not the most direct and efficient method, as it can take 9-13 synthetic steps to construct the key 9-membered ring from the Diels Alder product. Other methods, such as those by Lei, Tu, and Wang, focus on the construction of the 9-membered ring and the quaternary carbon simultaneously as a spirocycle. Lei utilized DBU to affect an intramolecular 1,3-dione alkylation, from which they could generate fawcettimine, fawcettidine, and 8-desoxyserratinine in 7 steps. Tu and Wang's syntheses used the chiral pool reagent (+)-pulegone as a starting material, and also a semipinacol rearrangement was developed to form the quaternary spirocenter. This allowed access to alkaloids (+)-alopecuridine, (+)-sieboldine A, and (-)-lycojapodine A.[69]

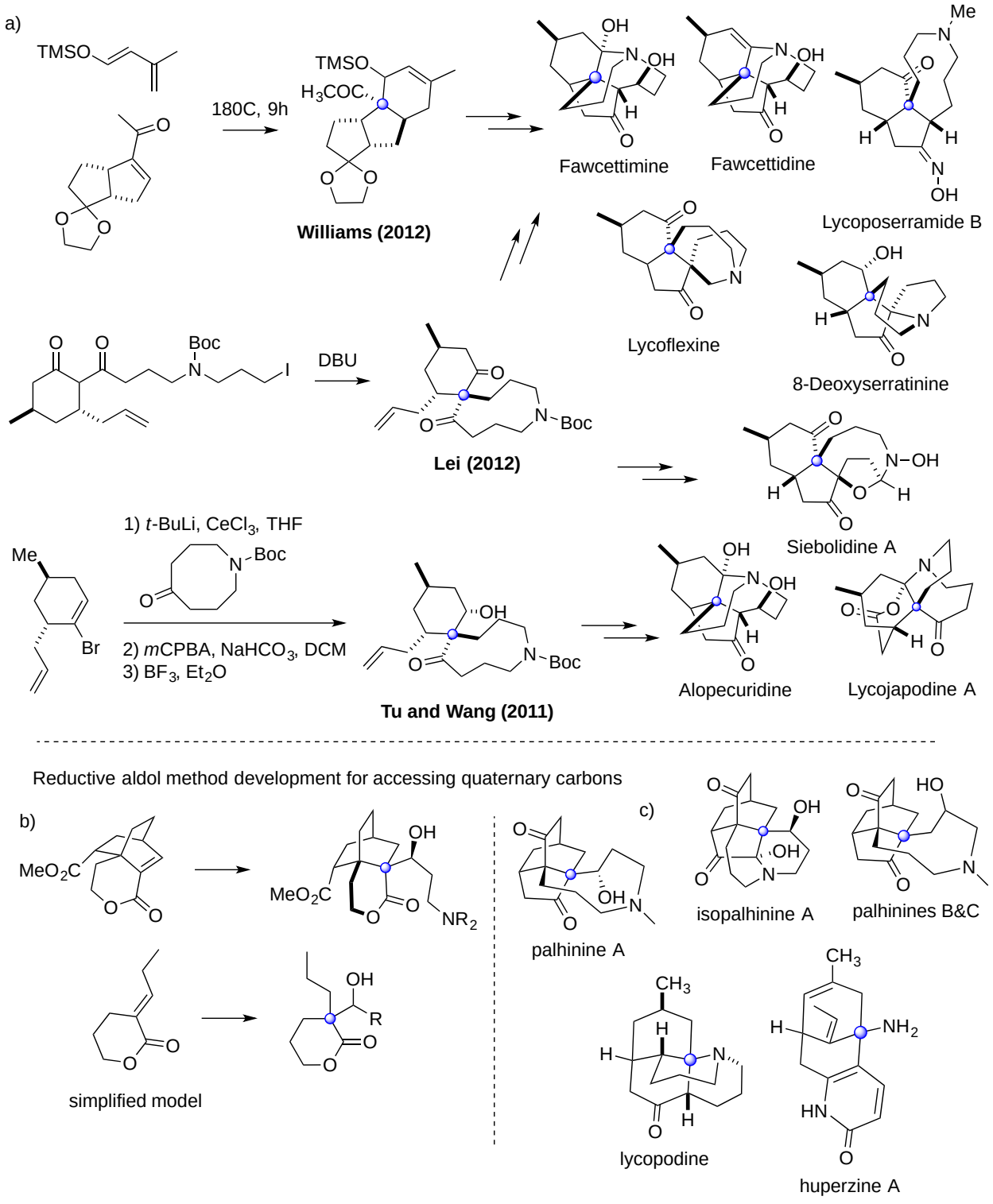



Figure 3.1 a) Strategies for generating quaternary carbons that can be elaborated into Lycopodium alkaloids. b) Quaternary carbon reductive aldol intermediate and model system. c) Lycopodium alkaloids, quaternary carbons emphasized.

These powerful methods have a proven utility towards broad groups of alkaloids. However, the palhinine and isopalhinine targets are increasingly complex because they contain a 6-6-6 bicyclic motif. These Heathcock-inspired strategies could be problematic to apply towards the palhinines, so we have pursued a new method for generating quaternary carbons – the reductive aldol. Discussed in Chapter II of this thesis, a Diels Alder reaction between methyl acrylate and a Birch reduction diene from isochromanone generates a quaternary carbon-containing bicyclic scaffold. This is followed by a reductive aldol reaction that generates an additional quaternary carbon adjacent. This reaction employs a unique electronically enhanced triarylphosphine oxide catalyst because we experienced difficulties and lower yields when using commercially available Lewis bases. Because we made this minor but significant and powerful alteration to the catalyst, we decided to develop this reaction as a general method and explore the substrate scope. Furthermore, before we had pursued the Birch reduction and Diels Alder steps of the total synthesis, we were exploring this method on a model tri-substituted lactone substrate. Based on differences between the palhinine and model systems, we were able to gain insight into the mechanism and substrate possibilities, which will be discussed in detail in this chapter, as well as supporting calculations in Chapter IV.

*Challenges and advantages of quaternary-specific methods*

The significance of this method – forming quaternary carbons – can be justified by the inherent difficulty but necessity to synthesize molecules of increasing complexity. Toxicity is known to be the leading cause for drug candidates failing clinical trials.[70] Recent studies suggest that compounds of higher complexity, as measured by the saturation and presence of $sp^3$-hybridized quaternary carbon centers, have fewer off-target effects, show less toxicity, and have a greater success rate in clinical trials.[71] However, synthetic access to molecules with increased complexity requires successful methods for the construction of quaternary carbon centers.[72] Despite recent advances, synthetic challenges in the formation of quaternary carbon centers still exist, and prove even more difficult when the desired quaternary carbons are chiral.[73]

Additionally, quaternary carbon centers in acyclic molecules and molecular fragments remain challenging to access.[74] Most of the methods currently available for the construction of quaternary carbons rely on metal-based catalysts, and the development of alternative catalytic systems was recently described as a future challenge.[75] Here we describe a method for the

diastereoselective construction of β-hydroxyl lactones and lactams bearing α-quaternary carbon centers, which relies on simple, electronically differentiated phosphine oxides as Lewis base catalysts. The strategy enables access to a structural motif that is prevalent in many biologically relevant target structures (Figure 3.2).

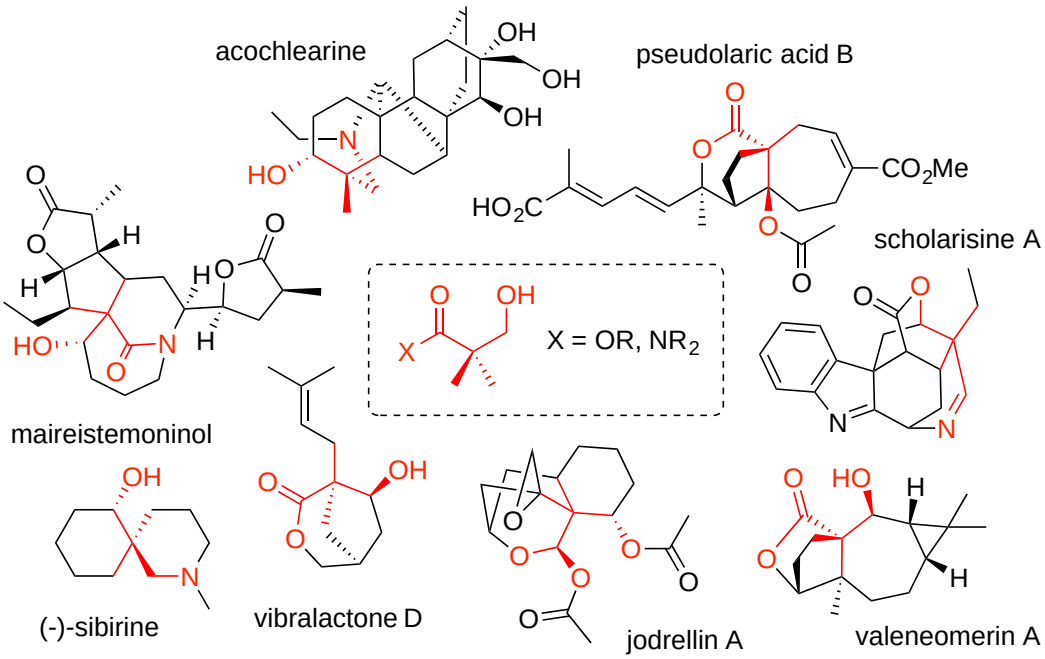



Figure 3.2 A cluster of natural products that contain a quaternary aldol motif or derivative.

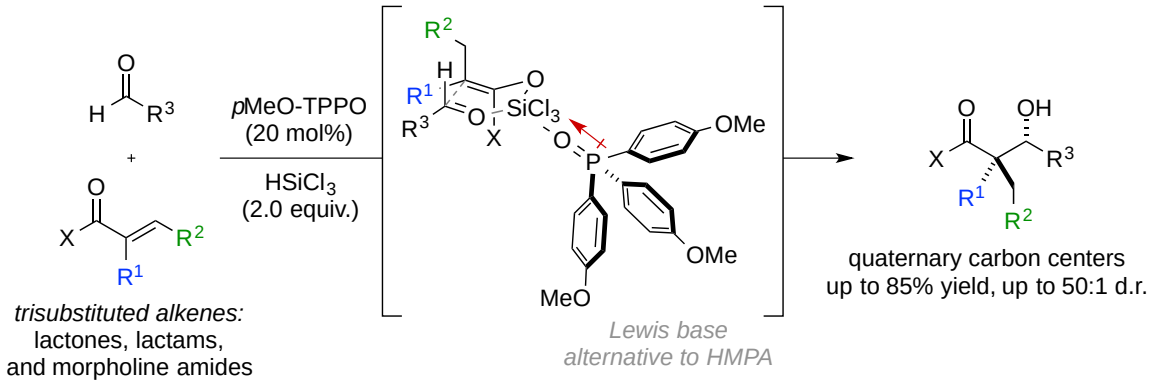



Figure 3.3 Method summary: a 1,1-disubstituted Michael acceptor and aldehyde reductively ($HSiCl_3$) combine to generate quaternary carbon centers, catalyzed by an electron-rich phosphine oxide.

The isopalhinine A synthesis project in our laboratory (Chapter II) required operational access to complex lactones bearing quaternary carbons from α,α,β-trisubstituted enones (Figure

3.3). A reductive aldol approach seemed particularly desirable, as it would permit a select Michael acceptor to react in the presence of enolizable functional groups such as esters. Several successful protocols for transition metal-catalyzed reductive aldol reactions for α,β-unsaturated carbonyl compounds have been described that use Rh,[76] Ir,[77] Cu,[78] Co,[79] Ru,[80] or Pd[81] in combination with boranes, silanes or hydrogen gas as reductants. Methods for converting α,α-disubstituted,[82] tri-,[83] and tetra- substituted enones to the reductive aldol products that are bearing α-quaternary carbons are less common (Figure 3.4).

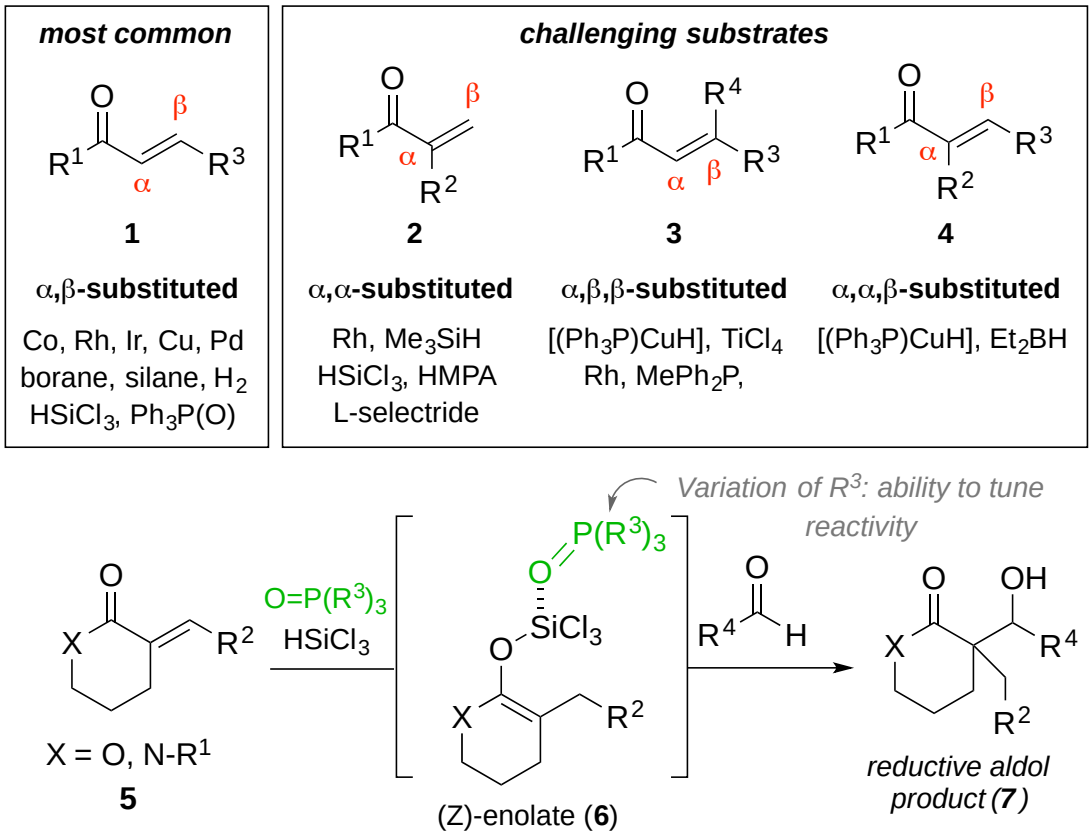


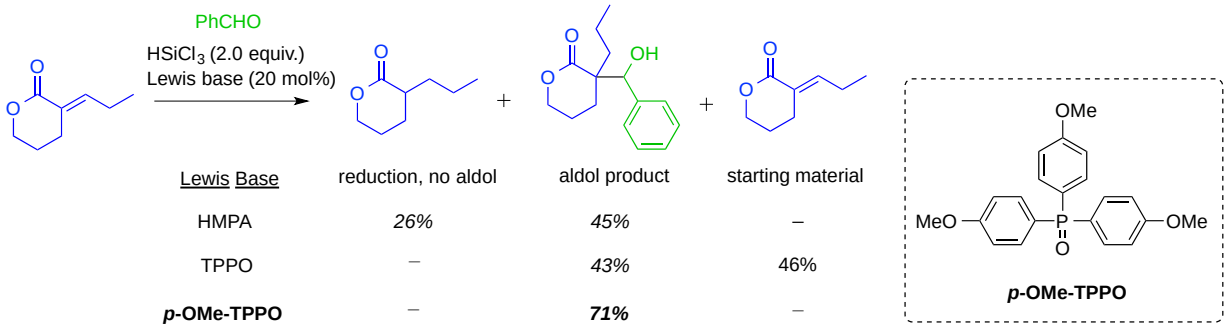

Figure 3.4 Most common enones for intermolecular reductive aldol reactions. We use a Lewis base catalyst for these challenging substrates because it can be tuned.

*Catalyst screening and reaction optimization*

An inherent challenge to highly-substituted enones relates to the identification of potent catalyst systems that 1) exhibit high levels of chemoselectivity for 1,4-reduction, 2) activate both the resulting enolate nucleophile and aldehyde electrophile for aldol addition while 3) minimizing competing reduction of the aldehyde electrophile. Denmark's pioneering work has

established Lewis bases as a powerful class of catalysts capable of enhancing enolate nucleophilicity in asymmetric aldol reactions.[84] Recently, Nakajima has shown that Lewis bases, such as TPPO and HMPA, are able to promote reductive aldol reactions of α,β-disubstituted enones, though α,α-disubstituted and trisubstituted enones still remain elusive as substrates.[85] We postulated that the reactivity of these Lewis base catalysts can be tuned to the specific electronic and steric requirements inherent to highly functionalized enones, to enable both in situ conjugate reduction and activation of the resulting enolate for a subsquent aldol reaction. Aryl phosphine oxide derivatives seemed particularly desirable Lewis bases, as they allow for facile electronic differentiation of the aryl substituents to probe our hypothesis.

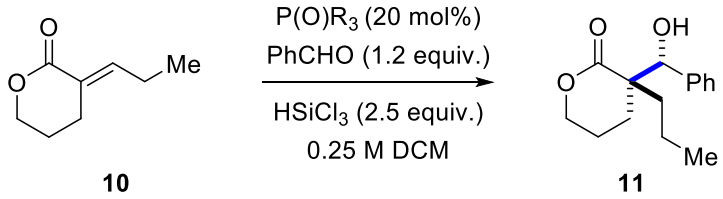
Table 3.1 Preliminary reaction profile catalyst evaluation on the model substrate.



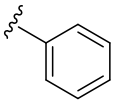
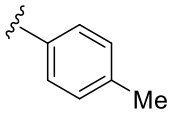
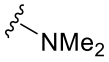
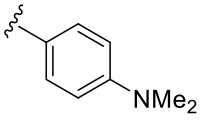
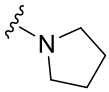
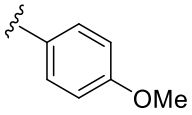
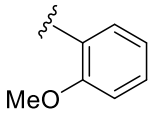
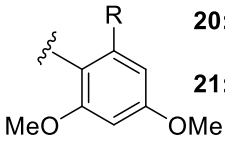

| Lewis Base | reduction, no aldol | aldol product | starting material |
|---|---|---|---|
| HMPA | *26%* | *45%* | – |
| TPPO | – | *43%* | 46% |
| ***p*-OMe-TPPO** | – | ***71%*** | – |

Our initial studies with the model lactone, bearing an exocyclic Michael acceptor, with benzaldehyde as electrophile and TPPO or HMPA as the Lewis base catalyst and using $HSiCl_3$ as the hydride source proved promising and resulted in the formation of the reductive aldol product **11** in 43% and 45% yield, respectively (Table 3.1). Although both catalysts produced aldol product in similar yields, the reaction profiles greatly differed. Starting material was recovered when employing TPPO, but was consumed with HMPA, forming both the 1,4-reduced lactone and benzyl alcohol as side products. These results suggest that HMPA is a potent catalyst for initial conjugate reduction but is too sterically encumbering to fully promote subsequent aldol reaction. In comparison, TPPO is not Lewis basic enough to be a productive catalyst for the initial conjugate reduction reaction thus resulting in recovered of starting material.

Table 3.2 Comprehensive phosphine oxide catalyst evaluation.




**10** **11**

| entry | R | | yield (%) | entry | R | | yield (%) |
|---|---|---|---|---|---|---|---|
| 1 |  | **12** | 43 | 6 |  | **17** | 39 |
| 2 |  | **13** | 45 | 7 |  | **18** | 37 |
| 3 |  | **14** | 0 | | | | |
| 4 |  | **15** | 49 | 8 |  | **19** | 71 |
| 5 |  | **16** | 23 | 9 |  | **20:** R= H | 18 |
| | | | | 10 | | **21:** R= OMe | 9 |

***Conditions:*** Reactions were ran in 0.25 M DCM at 30 °C for 48 hours with 1.2 equivalents of benzaldehyde.

Attempts to use the HMPA analogs **14** and **15** to decrease steric bulk in the aldol addition resulted in either no reaction or no improved yield of the desired reductive aldol product **11** (entries 3 and 4, Table 3.2). As a result, subsequent catalyst optimization centered on electronic differentiation of triaryl phosphine oxides to increase their reactivity in the initial 1,4-reduction. Lewis bases **16**, **20**, and **21**, bearing electron-donating substituents in the *ortho*-position, formed lactone **11** in low yields likely due to the increased steric bulk compared to TPPO (**12**) (entries 5, 9-10). Para-methyl triarylphosphine oxide **17** showed a reaction profile similar triphenylphosphine oxide (**12**) and resulted in the formation of **11** in 39% yield together with reisolated starting material (entry 6). In comparison, the corresponding Lewis base **18** bearing a dimethylamine moiety in the *para*-position, exhibited low solubility in dichloromethane and resulted in diminished yields of **11** (entry 7). However, *para*-methoxy triarylphosphine oxide **19**

led to formation of product in 71% yield with minor competing reduction (entry 8) and was chosen as the optimal Lewis base catalyst for this study.

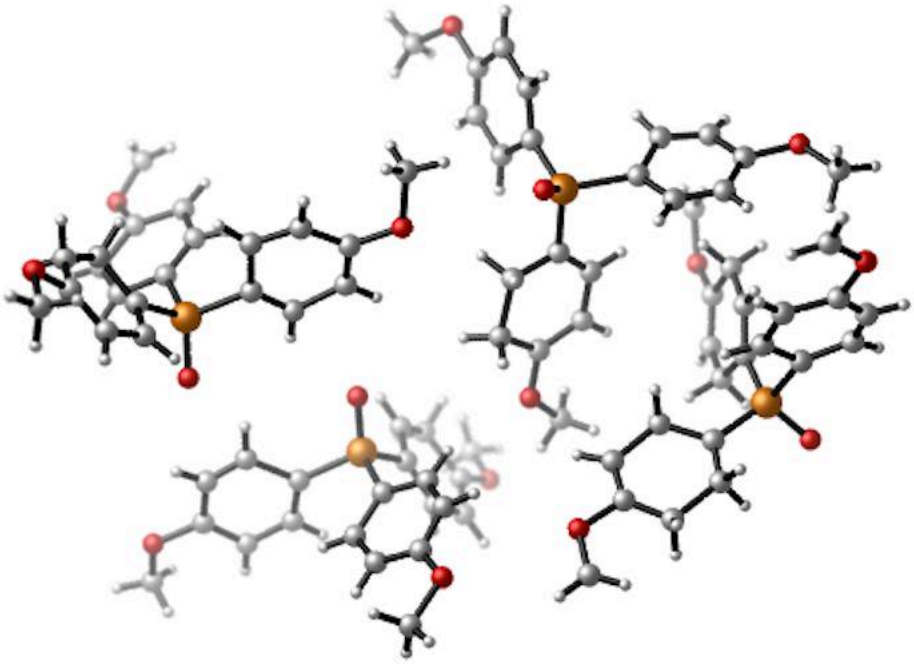


Figure 3.5 X-ray crystal structure of the *para*-methoxy phosphine oxide catalyst by Ren Wiscons of the Matzger group.

Subsequent reaction optimization focused on the silane reductant. It was found that 2.5 equivalents of trichlorosilane were optimal, while increased amounts resulted in diminished yields of the desired reductive aldol products due to competing reduction side-products. Additionally, 20 mol% catalyst loadings proved superior with minimal reduction of the aldehyde electrophile (<10%), while stoichiometric quantities of Lewis base **19** resulted in diminished yields of 28%. Notably, the diastereomeric ratio of aldol product **11** remained constant despite changes in catalyst loading.

*Diastereomers through different transition states*

Transition state models similar to those proposed by Denmark for phosphoramide-catalyzed aldol reactions of pre-formed trichlorosilyl enolates can justify the stereochemical outcome observed in the reductive aldol reaction.[86] Stereochemical models are consistent with a boat transition state **25** resulting in the major diastereomer **27** with both $CH_2R^2$ and hydroxyl substituent being *anti* to one another. The minor diastereomer with $CH_2R^2$ and hydroxyl group

being *syn* to one another is formed via boat transition state **26** (Fig. 3.6A). The relative configuration of both diastereomeric products of lactam **28** and tolualdehyde **29** was confirmed using x-ray analysis to result in the formation of lactam *anti*-**30** as the major diastereomer and *syn*-**31** as the minor diastereomer in a combined 70% yield (Fig. 3.6B).

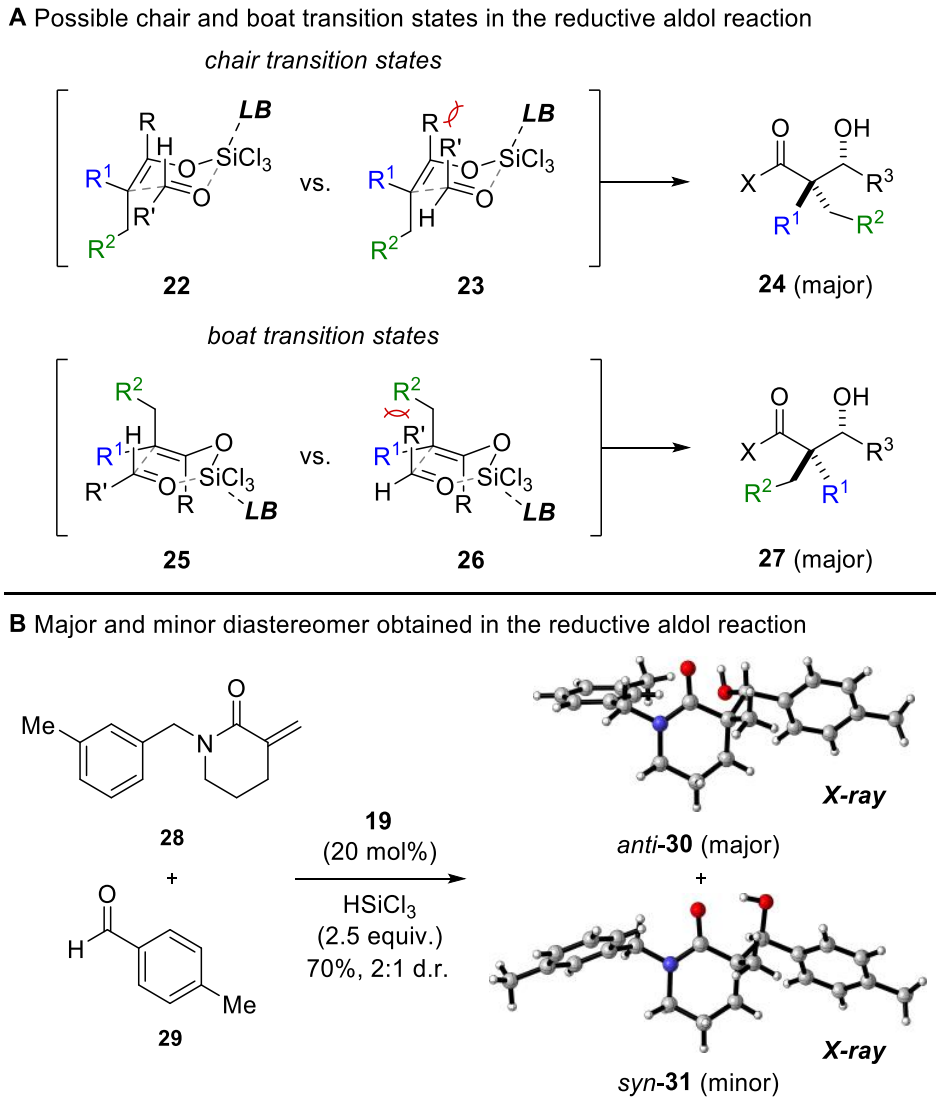
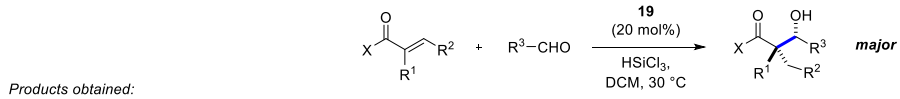
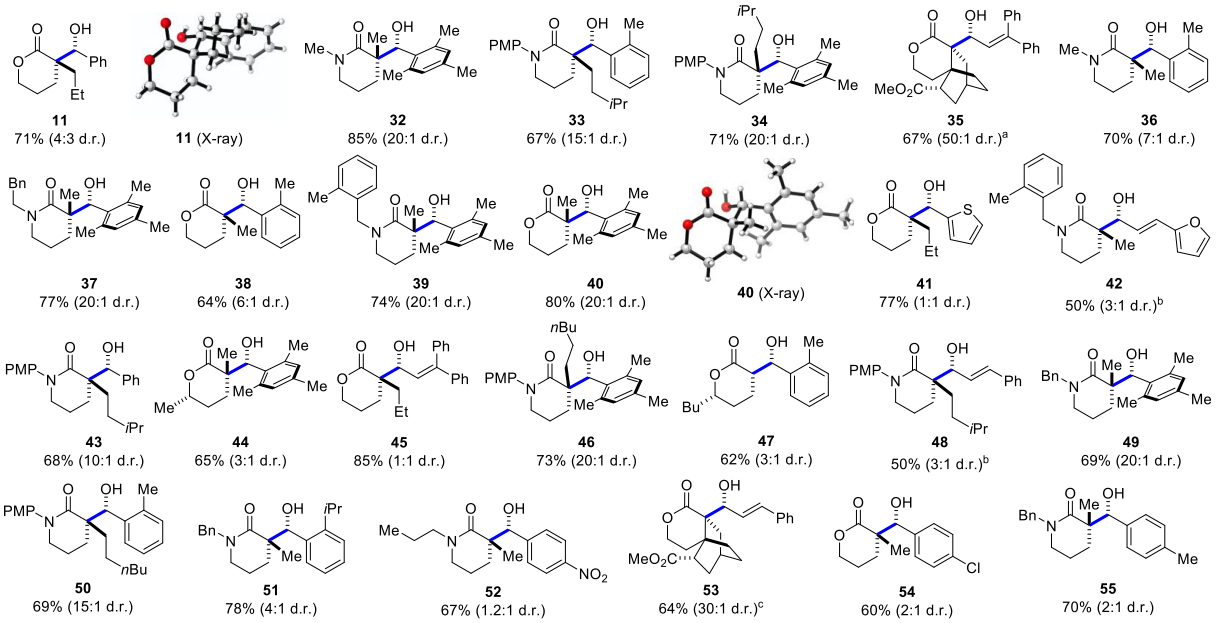



Figure 3.6 Transition state models and crystal structures for each of the diastereomers.

Table 3.3 A broad and general table of products obtained from the reductive aldol reaction.




*Products obtained:*




***Conditions:*** Michael acceptor (1 mmol), aldehyde (1.5 mmol), *p*OMe-TPPO (**19**, 20 mol%), $HSiCl_3$ (2.5 equiv.), in dichloromethane (0.25 M) at 30ºC for 48h; a) reaction is complete in 12h; b) in toluene (0.25M); c) aldehyde is added after 8h. Reaction is quenched 12h after addition of the aldehyde.

*Substrate scope and synthetic utility.*

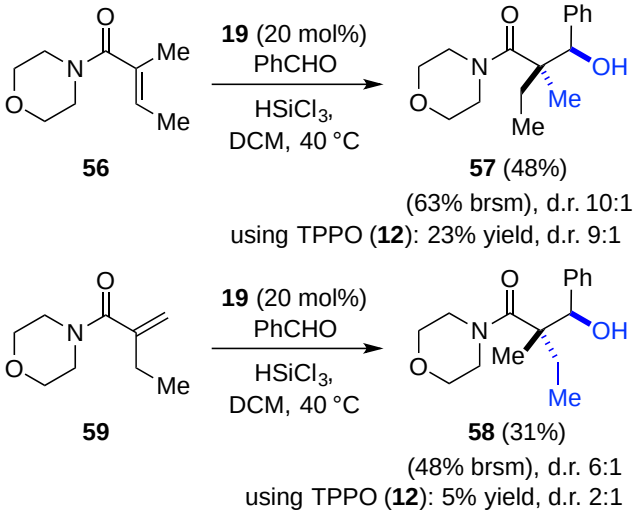
The conditions were efficient for construction of a variety quaternary carbon-bearing lactones and lactams, (Table 3.3) affording yields and diastereomeric ratios up to 85% and 50:1, respectively. For 6-membered monocyclic lactones and lactams, the anti-product was favored with diastereomeric ratios up to 20:1 d.r., increasing with both aldehyde and alkene bulk (**11**, **32**-**34**, **36**-**52**, **54**-**55**, Table 3.3). Importantly, sterically encumbered tricyclic lactones resulted in the formation of the corresponding hydroxylactones **35** and *53* in up to 67% yield and 50:1 d.r. N-alkyl- or N-aryl-substituted lactams worked under the optimized reaction conditions leading to high yields (85%) and diasteromeric ratios (20:1) of the desired products (**32**-**34**, **36**-**37**, **39**, **42**, **43**, **46**, **48**-**52**, **55**, Table 3.3). Lactams bearing para-methoxyphenyl (PMP) or benzyl protecting groups afforded high yields and good to excellent diastereomeric ratios of the desired hydroxylactams (**34**, **48**-**51**). Aryl aldehydes with varying substitution are viable electrophiles, and increased steric hindrance on the aromatic moieties lead to higher diastereomeric ratios (e.g.

**32**, **34**). Aldehydes conjugated to heterocycles including furan and thiophene were tolerated rendering yields up to 77% (**41**, **42**).

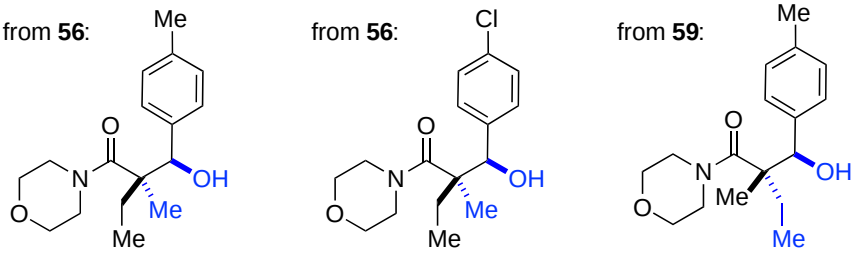
Initial efforts to extend the substrate scope to vinyl aldehydes, such as cinnamaldehyde, proved challenging due to the formation of competing aldol condensation products. However, conducting the reaction in toluene under otherwise identical conditions attenuated this competing self-condensation and resulted in decent yields of the respective hydroxylactone and lactam adducts (**42**, **45**, **48**, Table 3.3). Aliphatic aldehydes proved incompatible under the optimized reaction conditions resulting exclusively in the formation of the reduced substrates. Competing deprotonation of the aldehyde at the α-position occurs preferentially over formation of the enolate nucleophile (Figure 3.8).

Table 3.4 Morpholine amides as substrates for the reductive aldol.

**A** Reaction of morpholine amides:




**B** Selected products:




***Conditions:*** Michael acceptor (1 mmol), aldehyde (1.5 mmol), *p*MeO-TPPO (**19**, 20 mol%), $HSiCl_3$ (2.5 equiv.), in dichloromethane (0.25 M) at 30˚C for 96h.

Furthermore, morpholine amides **56** and **59** proved to be viable substrates (Table 3.4). Morpholine amides are important synthetic alternatives to Weinreb amides characterized by their ease of use.[87] Upon conversion of **56** with a variety of aldehydes under the optimized condition, the corresponding aldol products were obtained bearing a methyl group *syn* and an ethyl group *anti* to the hydoxyl group (**57**, **60**, **61**). Notably, the products of this reaction with our electronically-enhanced catalyst are formed in up to 60% yield and 10:1 d.r., while the use of TPPO resulted in overall diminished yields. Importantly, the products are diastereomeric to those obtained via an alternate approach relying on $(Ipc)_2BH$,[88] thus providing a valuable complementary synthetic alternative (**58**, Table 3.4A). The same observation was made for the conversion of **59** under the optimized reaction conditions, resulting in the formation of **58** and **62**, albeit in lower yields (Table 3.4).

The reductive aldol products are versatile building blocks bearing quaternary carbons (Fig. 3.7). Hyroxylactam **49** was reduced to its piperidine analog **63** in 96% yield in a two-step sequence. Also, hydroxylactone product **11** was converted upon treatment with $LiAlH_4$ to the corresponding triol **64** in 72% yield.

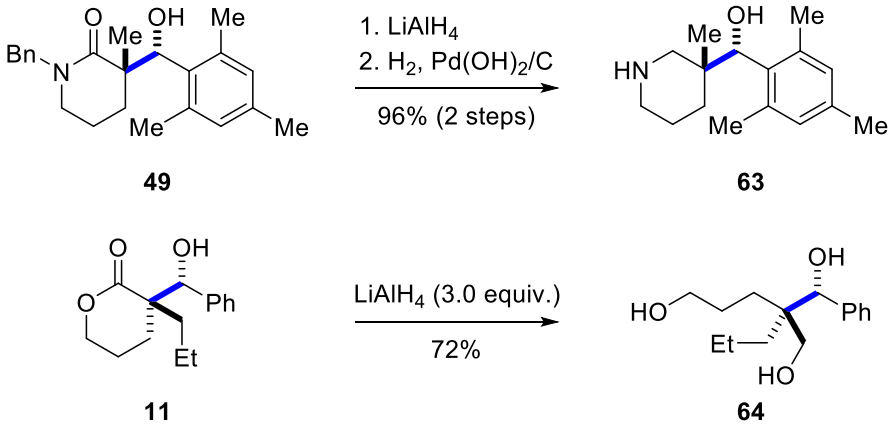



Figure 3.7 Transformations of reductive aldol products **11** and **49**.

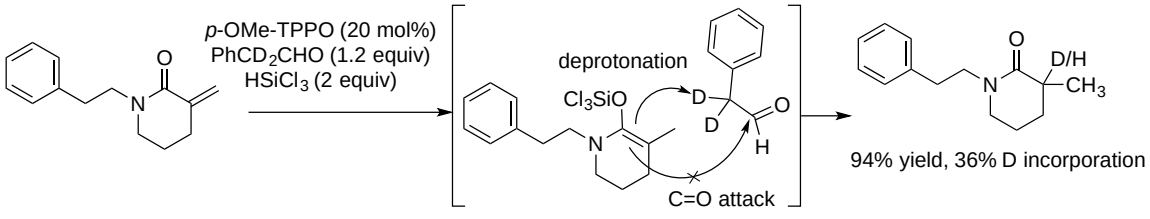



Figure 3.8 Deuterium incorporation by deprotonating an aliphatic aldehyde substrate.

*Summary & Future Directions*

A synthetic method for the efficient construction of β-hydroxylactones, -lactams and morpholine amides bearing α-quaternary carbon centers is described. The simple para-methoxy triarylphosphine oxide **19** was identified as a Lewis base catalyst uniquely effective in promoting the reductive aldol reaction of α,α-disubstituted and α,α,β-trisubstituted enones to form the quaternary carbon-containing products in up to 85% yield and 50:1 d.r. Importantly, this reaction exhibits complementary diastereoselectivity compared to those in the current literature.

Sections of this chapter are part of a manuscript; With no mention of isopalhinine A, this communication is currently submitted for review to *Organic Letters*. The supporting information and experimental details can be found as part of this publication with James Annand and Sukanta Bar. A collection of intermediates and products from Chapters II and III were submitted to the MScreen Center for Chemical Genomics database at the Life Sciences Institute. The physical samples have not yet been approved to be collected and are located in Chemistry 2632. Contact: Matthew O'Brien and Renju Jacob from CCG when these are ready to be submitted after publication of the *Organic Letters* paper.

## CHAPTER IV: Computational Investigation of Quaternary Lewis Base-catalyzed Reductive Aldol

*Abstract*

With the eventual goal of developing selective Lewis base catalysts, a racemic reductive aldol reaction was modeled. This multistep, multicomponent reaction that forms quaternary carbons was explored using Zstruct and growing string methods (GSM). Transition states uncovered using these methods showed the reaction to proceed around the Si center of the reagent $HSiCl_3$, operating through tetrahedral, trigonal pyramidal, and octahedral geometries. The Si center coordinates to the O of substrates and the catalyst. The Lewis base P=O, the lactone, and the aldehyde C=O bind to Si in a multitude of different geometries at the identified transition states, ultimately affording two diasteromeric aldol products. These mechanisms were modeled with various substrates and Lewis bases, and the calculated TS energies provide insight to experimental variations in rates and yields. Although the first step (reduction) generates a trigonal bipyramidal Si enolate complex with an approximate 120° O-Si-O geometry, catalyst dissociation is downhill, and subsequent catalyst re-coordination can occur to form more stable conformations. For all substrates, 90° is most stable, except for one 7-membered ring example that favors 180°. The most stable TS for the second step of the reaction (aldol) begins with a 180° O-Si-O enolate geometry (-11.3 kcal/mol), compared to the uncatalyzed reaction (-10.0 kcal/mol). The minor diastereomer could be a result of an uncatalyzed process (-10.0 kcal/mol), compared to the 90° TS energy (-6.3 kcal/mol), although the 180° TS energy (-9.7 kcal/mol) is so close that multiple mechanisms may be operative.

*Introduction*

The chemistry research community's continuous advancement of known structures and reactivity modes, combined with understanding from intense investigations of particular systems,[89] gives chemists the ability to create and control chemical reactions. Additionally, advances in theoretical chemistry and accessible modeling programs enhance the ability to visualize and predict reaction outcomes based on structural characteristics.

Automated reaction discovery methods can broaden chemical knowledge by finding new and unexpected reaction pathways.[90] In a recent investigation of automated computational methods,[91] for just a single molecule, 68 unique mechanisms were uncovered. Understandably, as a chemical system increases in complexity, a larger number of conceivable mechanisms could exist,[92] and this adds to the involvedness of studies if the goal is to map a large chemical system comprehensively. However, for synthesis purposes, when a particular molecule is a target, understanding all of the possible reaction outcomes is certainly remarkable, but not crucial for efficacious reaction development.

If a single product is preferred, highly coordinated transition states are required.[93] In their 2010 reference book *Enantioselective Chemical Synthesis: Methods, Logic, and Practice,*[94] chemists Corey and Kürti explain that there "…has been a dramatic increase in the possibilities for applying synthetic chemistry to human needs and well-being. However, a less favorable byproduct of recent progress is the ever-growing task for synthetic chemists to identify or select the most effective methods for solving a synthetic chemical problem." In other words, there are unlimited possibilities and nuances for controlling chemical space, so how can someone wisely pick what chiral ligand or catalyst could be effective for a particular enantioselective reaction?

Because enantioselective reactions are of fundamental importance in many industries,[95] unselective or achiral reactions are less directly practical. Industrial catalysis researcher Hans-Ulrich Blaser recalls, "In the early eighties, it became clear that racemic pharmaceuticals and agrochemicals would often be unacceptable to regulatory bodies and that enantioselective synthesis would become more and more important."[96] Perhaps not directly valuable, but still, an achiral reaction can be used as the starting point for developing selective variations.[97] From this initial result or set of outcomes, mechanistic hypotheses are tested to design a more favorable system, with the intent to increase the product yield and enantiomeric excess.[98] As Corey and Kürti state, "It is very important to have this knowledge of "pre-transition state" assemblies because it improves a synthetic chemist's ability to predict reaction product(s) and evaluate the suitability of a reaction for a particular application, thus elevating the power and precision of modern synthetic chemistry." Accordingly, computational modeling of transition states is a valuable device in developing and understanding enantioselective reactions.

In our circumstances, we have recently developed an achiral reaction that is catalyzed by a simple symmetric phosphine oxide Lewis base (Chaapter III). This first generation reaction

reductively combines Michael acceptors and aldehydes to form quaternary carbons (Figure 4.1c). It would be synthetically valuable to design and make catalysts that could achieve this reaction a) enantioselectively, b) with improved diastereoselectively, or c) more rapidly. In this work, mechanisms for the racemic quaternary reductive aldol reaction were investigated using relative energies from density functional theory (DFT) and growing string methods (GSM). These revealed transition states will provide a platform for the ability to judge potential reductive aldol catalysts *in silico*.

In addition to being racemic, the diastereoselectivity of the reaction is variable and not catalyst-controlled. The relative size of the substrates dictates the ratio of diastereomers (d.r.), and this selectivity increases with substrate bulk. For example, the relatively small benzaldehyde produces a d.r. of 2:1, while the bulkier, methyl substituted mesitaldehyde produces a d.r. of 20:1. In both cases, the major product has $–CH_3$ and –OH groups *anti* to one another. Ideally, we would like to find two different catalysts that can favor a select product, *syn* or *anti*, with high d.r., regardless of variations in substrate size.

Additionally, the reaction is limited by its substrate scope, which is currently restricted to specific Michael acceptor substrates that are fastened or poised into a reactive conformation where the carbonyl C=O and alkene C=C are positioned *syn*. Alpha-methenylated lactone and lactam rings were used as model substrates, and we observed that reactivity is modified by ring size (6 > 7 > 5). Pleasantly, a substrate where multiple rings are fused to the core, as might occur during a complex molecule synthesis, is more reactive than the monocyclic lactone. Strain brought on by the Michael acceptor being geometrically forced in a higher energy state by additional rings is relieved by reduction, thus decreasing the transition state barrier for that substrate. We hypothesize that linear substrates such as morpholine amides may be positioned to react because of steric bulk that favors the *syn* conformation. A more powerful Lewis base or differently shaped catalyst is needed to expand the substrate scope, which would make the reaction generally applicable towards routine linear molecules, different ring sizes, and consequently total synthesis of natural products.

Making quaternary carbons for natural products was the reason that we developed this reaction, and its underlying interactions of Lewis bases and silyl enolates have been reviewed extensively.[99] Denmark has studied Lewis base-catalyzed aldol reactions of trichlorosilyl enolates[100] (Figure 4.1a). Generally, these trichlorosilyl enolates are synthesized from their

parent ketone or ester, purified by distillation, and then subjected to aldol reactions with the catalyst and aldehyde.[101] Conversely, during our reaction, the enolate is formed *in-situ* by hydride addition from trichlorisilane, catalyzed by the Lewis base[14] (Figure 4.1c). In this case, the catalyst serves a dual role: a) to activate trichlorosilane and the Michael acceptor substrate for hydride addition to make the enolate; and b) to promote or allow an aldol reaction between the enolate and an aldehyde partner.

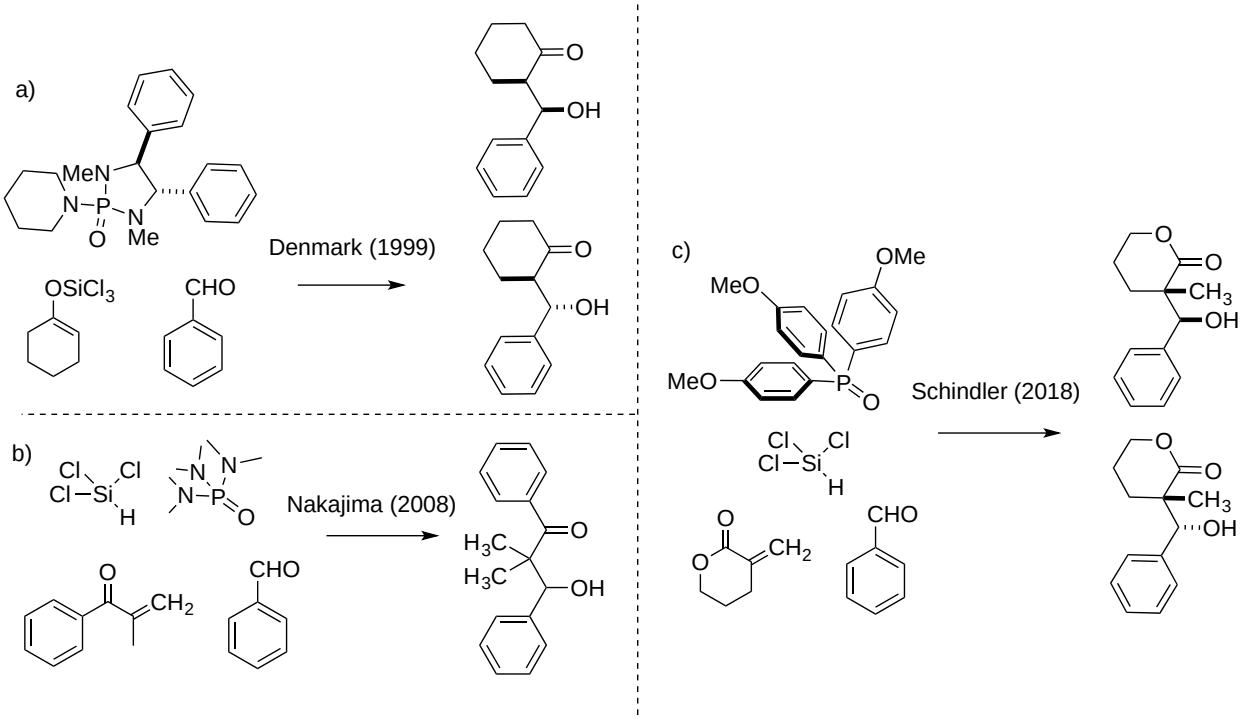



Figure 4.1 a) Denmark's phosphoramide-catalyzed aldol reactions, b) Nakajima's HMPA-catalyzed reductive aldol – single example of a quaternary product, and c) our *p*OMe-TPPO-catalyzed quaternary reductive aldol for lactones.

Denmark's work centers on phosphoramide catalysts. This type of Lewis base was problematic for our quaternary reductive aldol. In our system, the simple phosphoramide HMPA showed suitable activity for the first step (reduction), fully reducing the Michael acceptor substrate, but only gave modest (<50% yield) aldol product. The remaining material was the reduced lactone, indicating that the second step (aldol) was incomplete. Considering other Lewis base types, we thought aryl phosphine oxides could be effective. Following Nakajima's reductive aldol procedure,[102] we tried TPPO as a catalyst, but the reaction was slow, giving only 40% yield of product and 30% recovered starting material after 48 hours. However, the absence of reduced

lactone indicated that the second step of the reaction (aldol) was operating more efficiently with this aryl phosphine oxide compared to HMPA.

Our lactone substrate (43% aldol yield after 48 hours at 30°C) seemed to be inherently less reactive than Nakajima's chalcone substrate (78% aldol yield after only 4 hours at 0°C) with the same TPPO catalyst. In an attempt to optimize the reaction for our less-reactive substrate, we synthesized electron-rich tri-aryl phosphine oxides as new catalysts. For our system, they were able to mimic the strength of a phosphoramide, fully reducing the Michael acceptor, but with reduced steric interactions, allowing the aldol product to form fully (>80% yield). Additionally, Denmark's focus has been on tertiary products, but we are specifically targeting quaternary carbons. Therefore, an electron-rich aryl Lewis base is more effective for our purposes because of reduced steric interactions compared to phosphoramides. In terms of quaternary carbons, Nakajima only reported one example in 39% yield with HMPA (Figure 4.1b). They expanded the method to be enantioselective with tertiary carbons.[103] Consequently, we may not be able to apply the same chiral catalysts, rate laws, and transition states from Denmark and Nakajima's studies directly to our system.

This work models transition states for individual substrates, comparing their associated relative enthalpies with experimental reaction outcomes. The same comparison is done for different catalysts. Many variations can be assessed for the relatively straightforward 1,4-reduction. However, the aldol step gives an inherently more complex set of possible transition states because of catalyst placement geometric possibilities, so this was modeled with a more focused set of substrates and catalysts. The aldol calculations serve the purpose to elucidate the potential mechanisms for aldol addition, which could be uncatalyzed or promoted by the Lewis base in a variety of catalyst placement geometries.

## Computational Details: Materials & Methods

*Reduction*

Reaction discovery tools developed by the Zimmerman group were used to explore possible mechanisms of the principal reaction. At the beginning of the investigation, Zstruct was used to sample a combinatorial set of hypothetical reaction pathways, followed by single-ended growing string method (SE-GSM) of chosen reasonable actions.[104] For the first step, reduction, the aldehyde component was omitted because it is not involved yet. Also, the catalyst and silane were coordinated together as a single unit in order to reduce the number of Zstruct outcomes

generated with the Michael acceptor, α-methylene-δ-valerolactone. Our chosen frozen and active atoms are shown in Figure 4.2a. These choices were based on our proposed understanding of the reaction by Nakajima, in addition to an active chlorine atom to include the possibility that the mechanism could be ionic. Fortunately, the lowest energy outcome from this process (Figure 4.3, pathway F) was the expected reduction mechanism. We recognized this as a favorable route; the starting structures were varied in regards to Michael acceptor substrate and catalyst. Then, GSM was used to find analogous pathways (Figures 4.4 & 4.5) for these various structures.

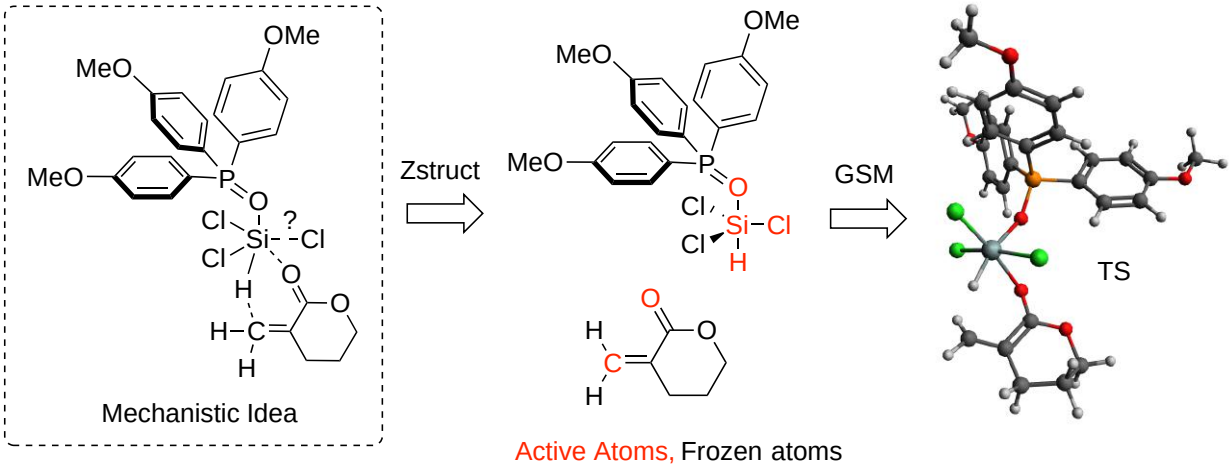



Figure 4.2a First transition state (reduction) found using Zstruct and GSM directed by a tentative mechanism idea.

*Aldol*

The second step of the reaction, the aldol, was investigated both as catalyzed and uncatalyzed. To begin, the product of pathway F and the electrophile benzaldehyde were subjected to the Zstruct method, followed by SSM. Unfortunately, the predicted catalyzed aldol mechanism was not uncovered during this first attempt, but instead a step where the catalyst dissociates from the Si center was revealed (Figure 4.3, pathway G). From this intermediate, we removed the catalyst and added the electrophile, benzaldehyde to model an uncatalyzed aldol mechanism. After running Zstruct and SSM, several pathways were revealed, including four similar pathways that generate the major diastereomer (2.1 d.r., Figure 4.7). The minor diastereomer was not indicated during this process, but could be uncovered by altering the successful input structure that generated the major product (Path P, Figure 4.7) by interchange of

the H and Ph groups. These transition state structures are depicted in Figure 4.8. Supplementary transition states were found with the corresponding bulky aldehyde, 2,6-dimethylbenzaldehyde (20:1 d.r., Figure 4.9) with the purpose to compare relative differences in transition state energies between diastereomers for the two different electrophiles.

Because the catalyst can dissociate from the Si-enolate, we can consider different geometry options for catalyst placement during the aldol step. After reduction, the enolate O and catalyst P=O (O-Si-O) angle is approximately 120°. Both substituents are equatorial in trigonal bipyramidal geometry. Other options include a catalyst-axial 90°, catalyst-equatorial 90°, or 180° position. These distinct geometries could be formed by either stepwise catalyst dissociation and re-coordination or possibly molecular rotations.

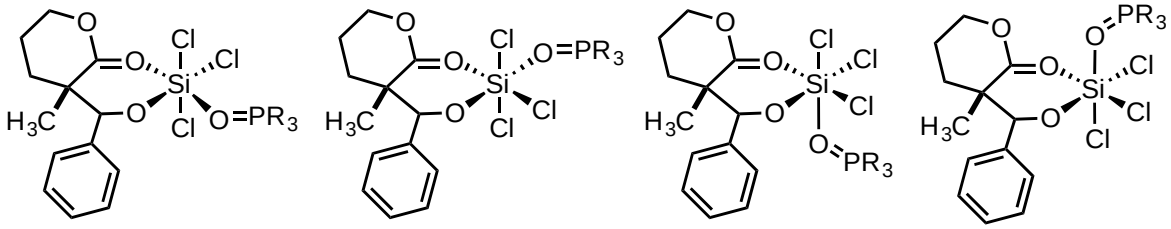


Figure 4.2b GSM input for catalyzed aldol. For a single product, four catalyst placements are plausible.

To find the catalyzed aldol mechanism, we began from proposed ending structures (Figure 4.2b) and drove the reaction backwards. Ongoing calculations aim to explore and compare all of the different possible geometries of enolates, transition states, and products for the aldol step.

## Results & Discussion

*Zstruct & GSM: Reduction*

In addition to the anticipated lactone O-Si coordination and hydride addition (pathway F, Figure 4.3) that forms a 120° enolate, Zstruct followed by GSM uncovered some distinct pathways from the starting structures. Pathway D, where the lactone C=O coordinates to the Si center and the catalyst P=O dissociates, have a low activation energy (+4.0 kcal/mol), but the product (-1.0 kcal/mol) is about 20 kcal/mol less stable than the enolate from path F (-21.2 kcal/mol). This equilibrium may be present, but does not lead to product formation. Additionally, path E led to catalyst dissociation from the silane, which can be used to backwardly model the catalyst and silane coordination prior to reduction. In path C, a chlorine atom dissociates (+13.6

kcal/mol) at a slightly smaller activation energy compared to the aldol step (+14.7 kcal/mol), indicating that chlorine dissociation is reasonable in energy, and the reaction could proceed as cationic. A higher energy pathway B (+27.2 kcal/mol) is the addition of a H radical rather than H hydride, creating a Si radical, and the highest energy pathway A (+49.9 kcal/mol) is the trichlorosilane H protonating the lactone C=O.

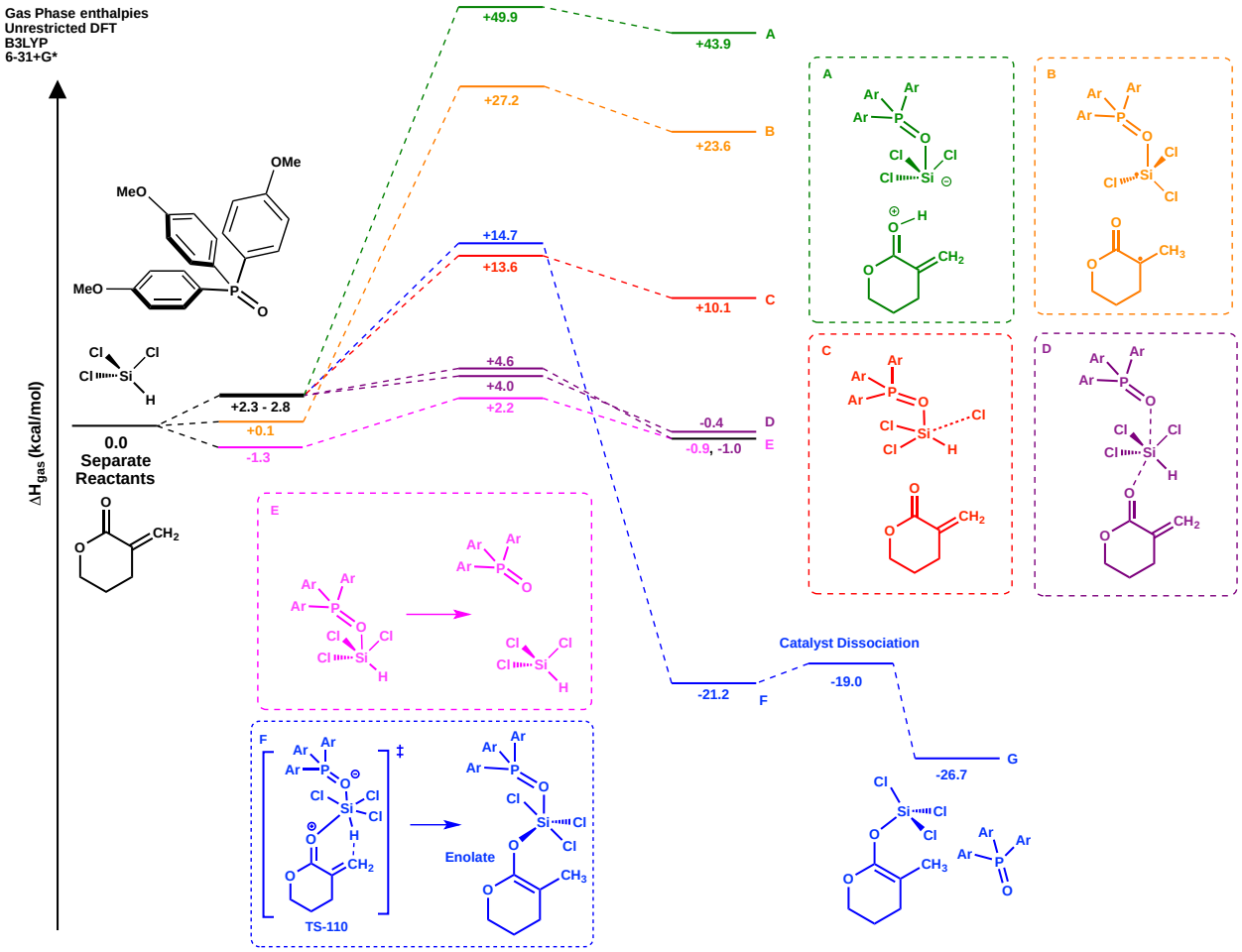


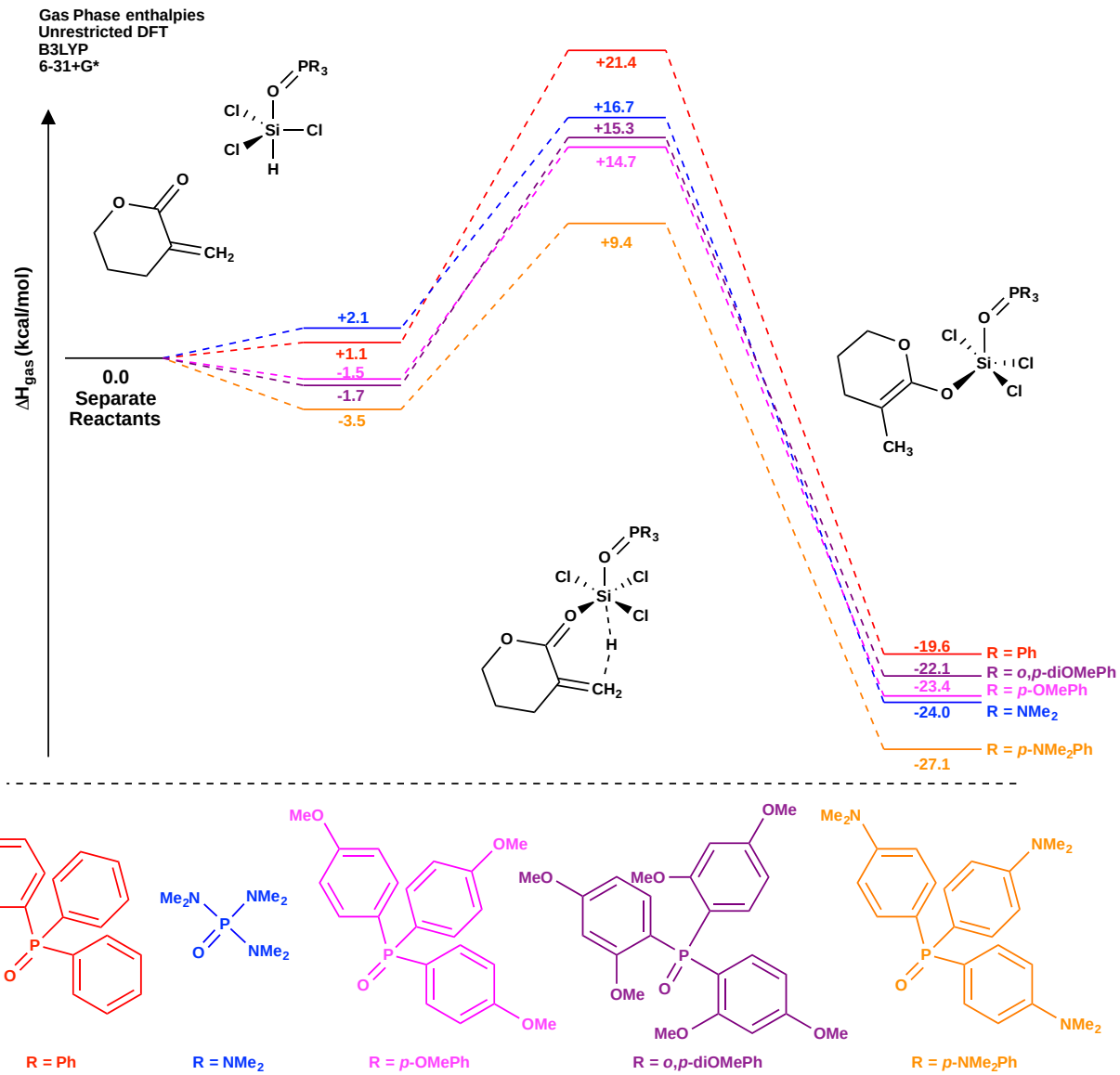

Figure 4.3 Reasonable reaction outcomes from Zstruct and SMM for *p*OMe-TPPO-catalyzed 1,4-reduction of the Michael acceptor lactone.

Among these pathways, intermediates B, C, and F were further pursued. From intermediate F, catalyst dissociation from Si (path G) was found to have a small activation energy (+2.2 kcal/mol) and the resulting tetrahedral trichlorosilyl enolate was even lower in energy (-26.7 kcal/mol). From intermediate C, removal of the floating Cl followed by SSM acquired the reduction step with 2 Cl's about Si, though it had activation energy of +34.2 kcal/mol, which was higher than the reduction with 3 chlorine atoms (See Supporting

Information). This suggests that the reduction most likely occurs as neutral and not cationic. Continued growth of intermediate B led in multiple cases to the coordination of the C=O lactone and the Si center, forming an enolate with 180° O-Si-O geometry rather than the 120° geometry found from String 110. In later calculations (Tables 2.1 & 2.2), these possible geometries, as well as two other possible 90° options, are contemplated for the aldol step by comparing their relative energies. However, for the reduction step, an energy barrier difference of 12.5 kcal/mol suggests that the radical pathway is not operative, since a 180° enolate could be formed by hydride addition (TS F) followed by catalyst dissociation (G) then association/isomerization, and less likely through the higher energy transition state B.

*Reduction: Catalyst Comparison*

After establishing a reasonable pathway for forming the enolate (F), relative energy comparisons of different catalysts (Figure 4.4) and substrates (Figure 4.5) were surveyed. The relative energies of our calculated transition states verify our hypothesis that electron-rich phosphine oxides can increase the rate of reduction. The slowest and most electro-neutral catalyst, TPPO, has the highest activation energy of +21.4 kcal/mol. In the mid-range are HMPA (+16.7 kcal/mol) and mono- an di-OMe-substituted aryl phosphine oxides (+14.7 kcal/mol and +15.3 kcal/mol, respectively. The predicted best catalyst (+9.4 kcal/mol TS) has the most electron-donating substituents with no additional size burden.


Gas Phase enthalpies
Unrestricted DFT
B3LYP
6-31+G*
ΔH gas (kcal/mol)
0.0
Separate
Reactants
+2.1
+1.1
-1.5
-1.7
-3.5
+21.4
+16.7
+15.3
+14.7
+9.4
-19.6
-22.1
-23.4
-24.0
-27.1
R = Ph
R = o,p-diOMePh
R = p-OMePh
R = NMe2
R = p-NMe2Ph


R = Ph
R = NMe2
R = p-OMePh
R = o,p-diOMePh
R = p-NMe2Ph

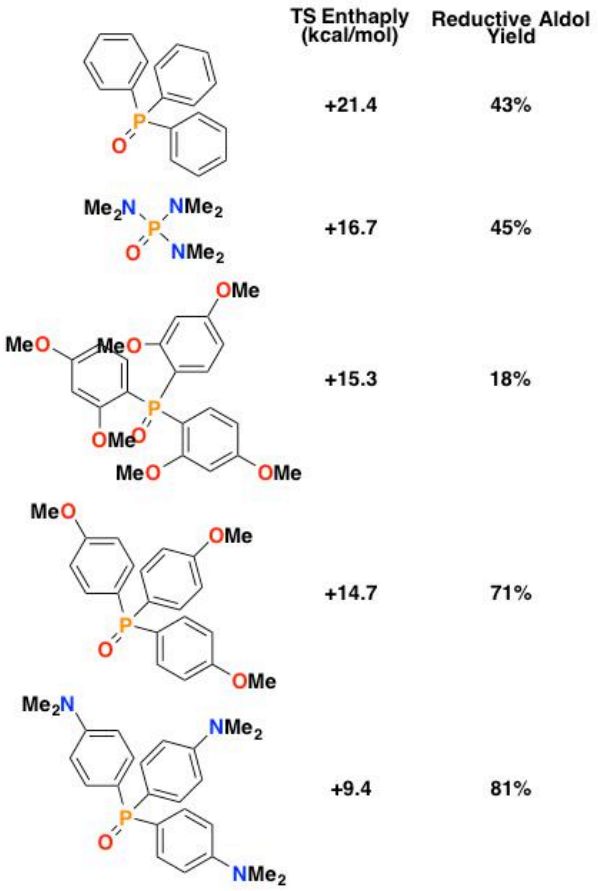



Figure 4.4 A comparison of Lewis base catalysts for the 1,4-reduction step using GSM.

*Reduction: Substrate Comparison*

Although overall, 6-membered ring substrates took 48 hours to fully react, subtle differences in reactivity could occur that can rationalize subtly lower yields.[105] According to GSM-found transition states, the N-methyl lactam substrate (pathway H, TS = +18.7 kcal/mol) is predicted to be less reactive than the lactone substrates. This is consistent with our results because N-methyl substrate was the lowest yielding lactam substrate. Interestingly, the 7-membered ring lactone substrate I, although low-yielding experimentally (<20% yield), was calculated to be about the same energy as the 6-membered ring F for the reduction step (+14.1 kcal/mol). This leads us to consider that either the starting material was impure for that reaction, or the aldol step was problematic. Apart from these slight substrate variations among monocyclic systems, a stark difference was computed for a strained bicyclic substrate. Delightfully, the natural product substrate K has negative activation energy (-1.9 kcal/mol), and this is evidenced by its rapid reduction (4-8 hours compared to 2 days).

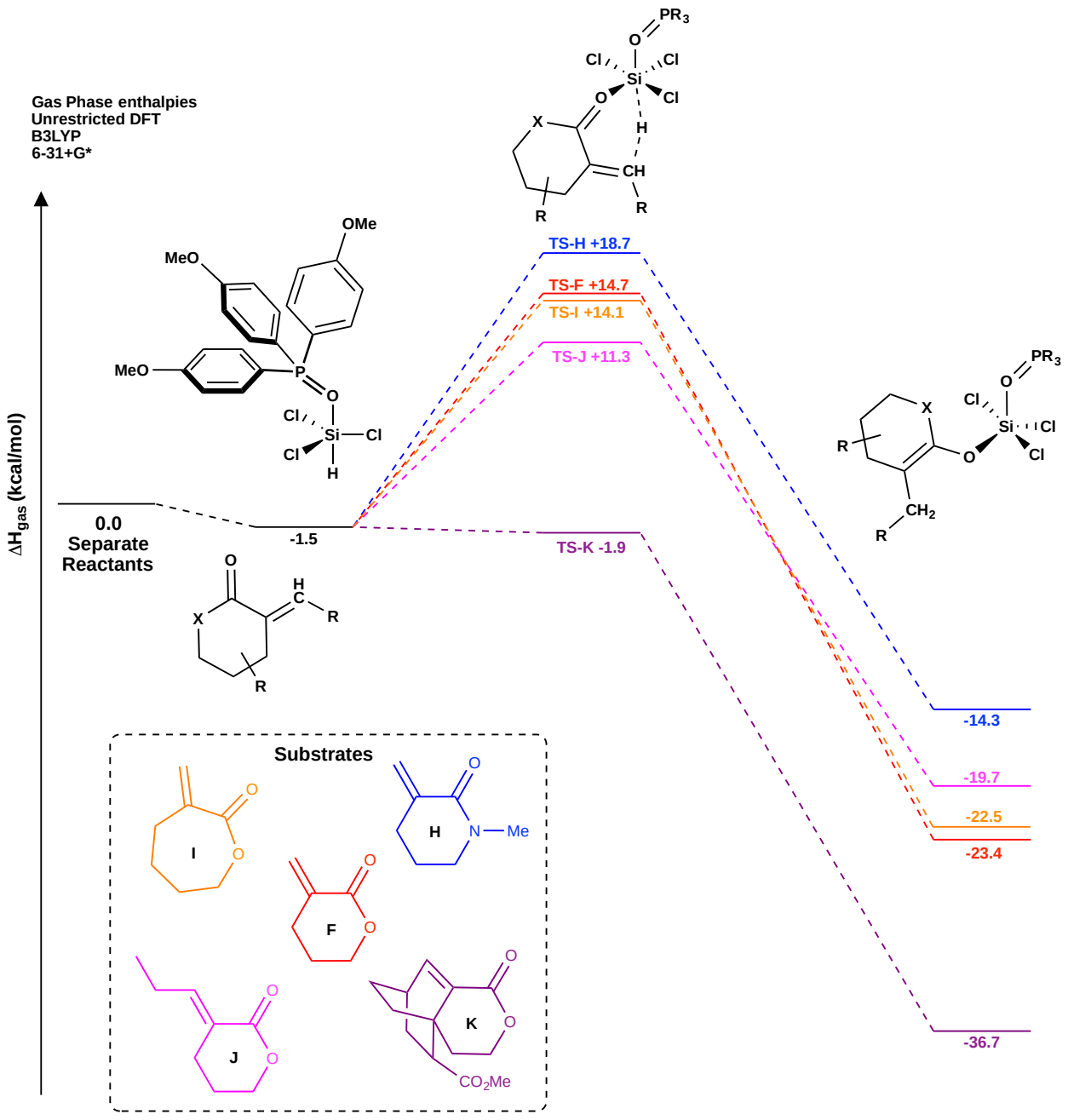



Figure 4.5 A comparison of Michael acceptor substrates for the 1,4-reduction step using GSM.

Using this especially reactive substrate K as an example, we looked more closely at different possible geometries and catalyst placements for the 1,4-reduction. Because this substrate is asymmetric, one could imagine the hydride delivery occurring from either the top or bottom face of the substrate. From the top face, the additional ester moiety faces downwards

away from the catalyst-silane complex (Figure 4.6, TS-K & TS-Ka). For reduction from the bottom face, the ester points towards the catalyst-silane complex (Figure 4.6, TS-Kb & TS-Kc).

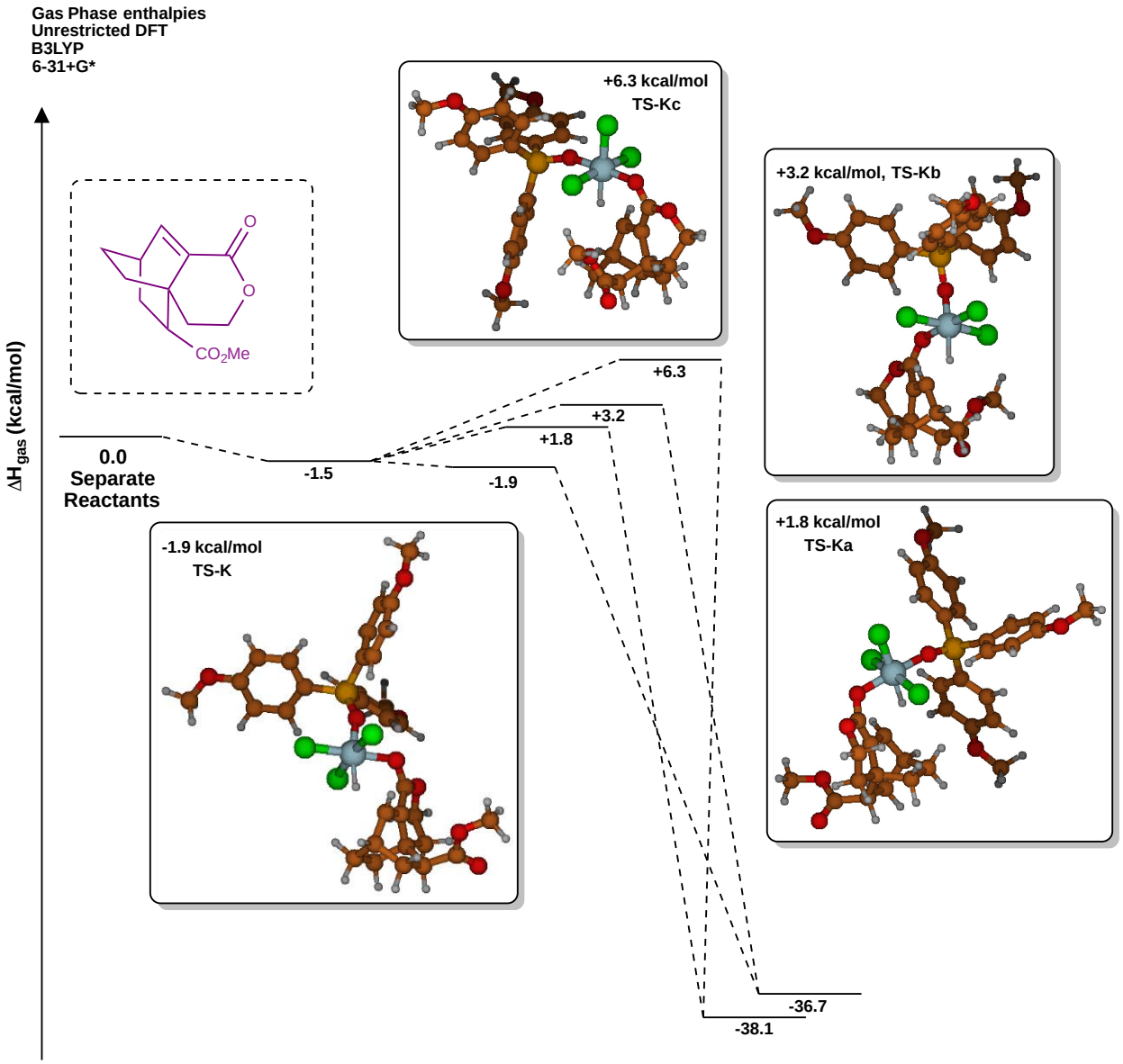



Figure 4.6 Four possible reduction TS for the asymmetric substrate found with GSM.

In addition to substrate asymmetry, there could be different possibilities for catalyst placement. In the example found with Zstruct, the catalyst is positioned 180° from the hydride, with the substrate C=O 90° in between the hydride and O=P (TS-K). This was found because the catalyst and silane were judiciously positioned 180° from each other for the Zstruct reaction

input. Another option is to have the catalyst and substrate 180° with the hydride 90° in between, which was found with GSM beginning with a 180° enolate geometry, using reaction coordinates to drive back to the starting material (TS-Ka & TS-Kc). As shown in Figure 4.6, the "bottom face" reductions are less favorable than "top face", and a 90° O-Si-O angle (TS-K & TS-Kb) is more favorable than the 180° possibility. In summary, the TS found with Zstruct and GSM was lowest in energy compared to other possible TS structures.

*Zstruct & GSM: Aldol*

The uncatalyzed aldol reaction was investigated with benzaldehyde using Zstruct. Much like the results from the first step, Ztruct followed by SE-GSM was able to find multiple pathways. The anticipated aldol step, which forms the major diastereomeric product, was lowest in energy (-11.6 kcal/mol TS, Figure 4.7, Pathway P). Interestingly, a few other distinct pathways were uncovered with this approach. With a TS energy of +10.4 kcal/mol, the aldehyde C=O coordinates to the Si, simultaneously breaking the Si-O bond of the lactone substrate (Pathway L). Aldehyde coordination without lactone dissociation was lower in energy (Pathway M, -2.2 kcal/mol TS E). Aldehyde coordination to Si could also promote the lactone enolate O to attack the C=O of the aldehyde, leading to formation of an acetal species (Pathway N, -5.5 kcal/mol). Similarly, a Cl from the enolate could attack the aldehyde C=O, resulting in a chlorinated alcohol (Pathway O, -0.3 kcal/mol). These products were not observed experimentally, but could perhaps be targeted if needed for new reaction development.

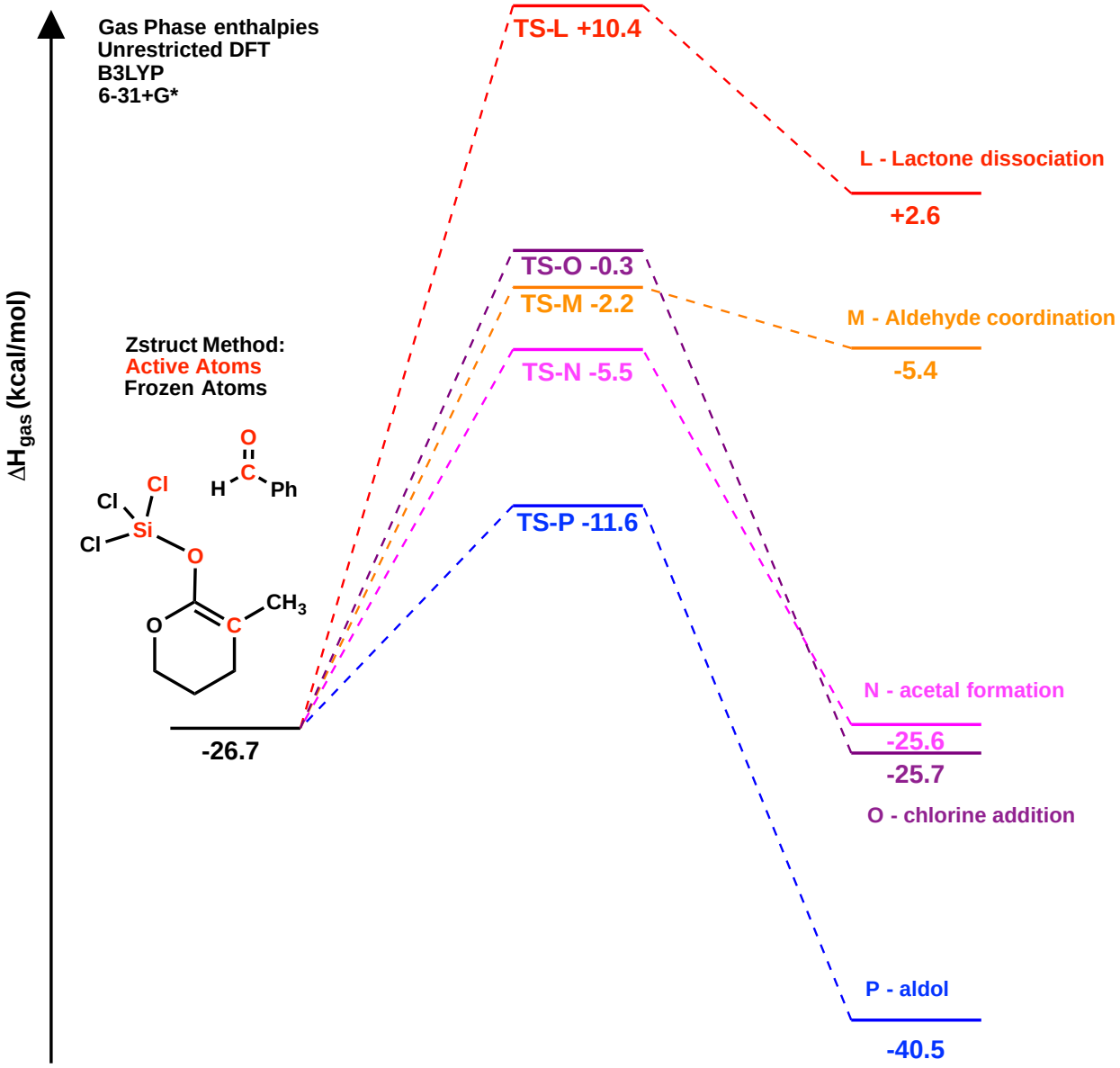
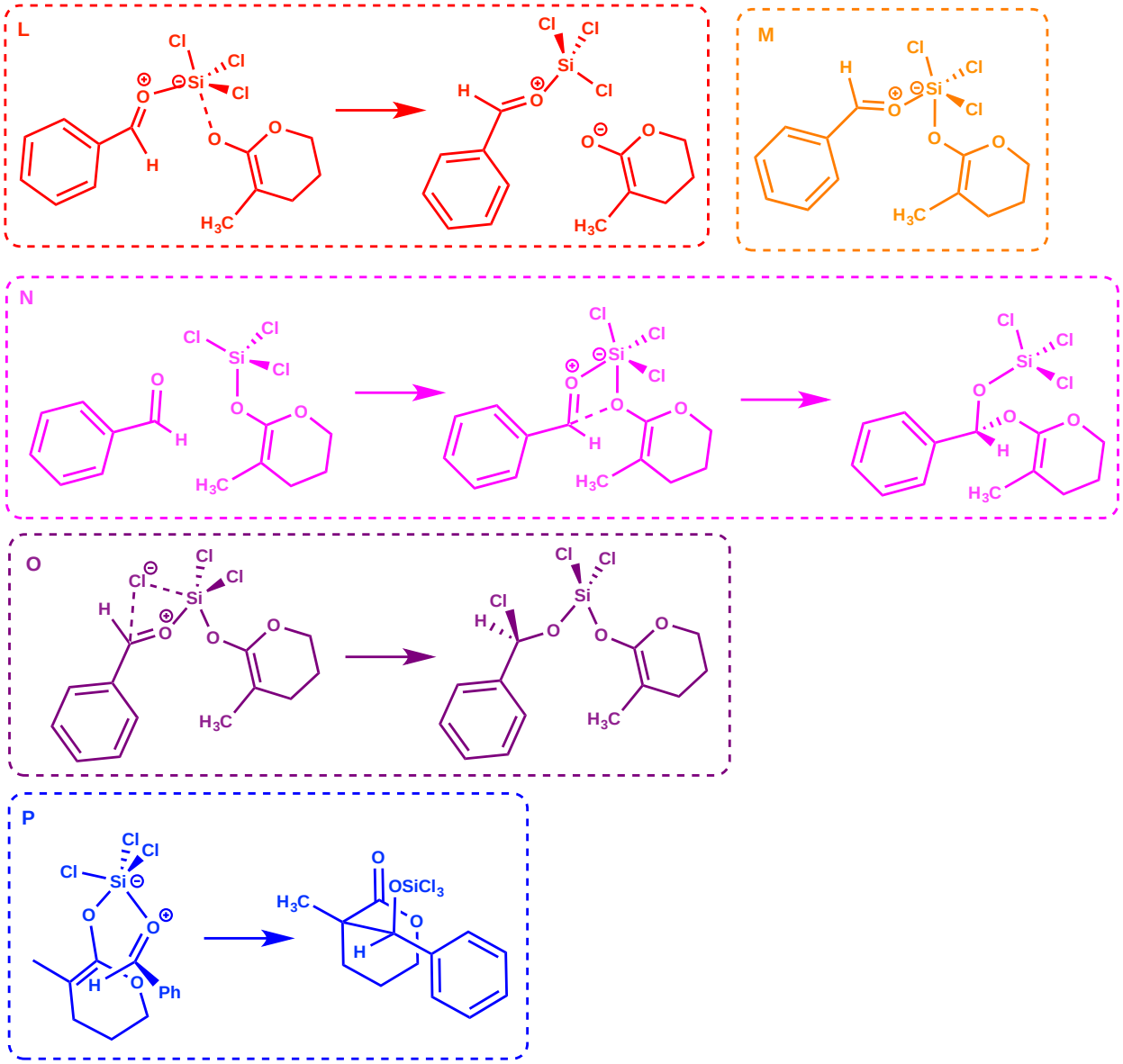



Figure 4.7a Reasonable reaction outcomes from Zstruct and SMM for an uncatalyzed aldol with the trichlorosilyl enolate and benzaldehyde.


L
M
N
O
P

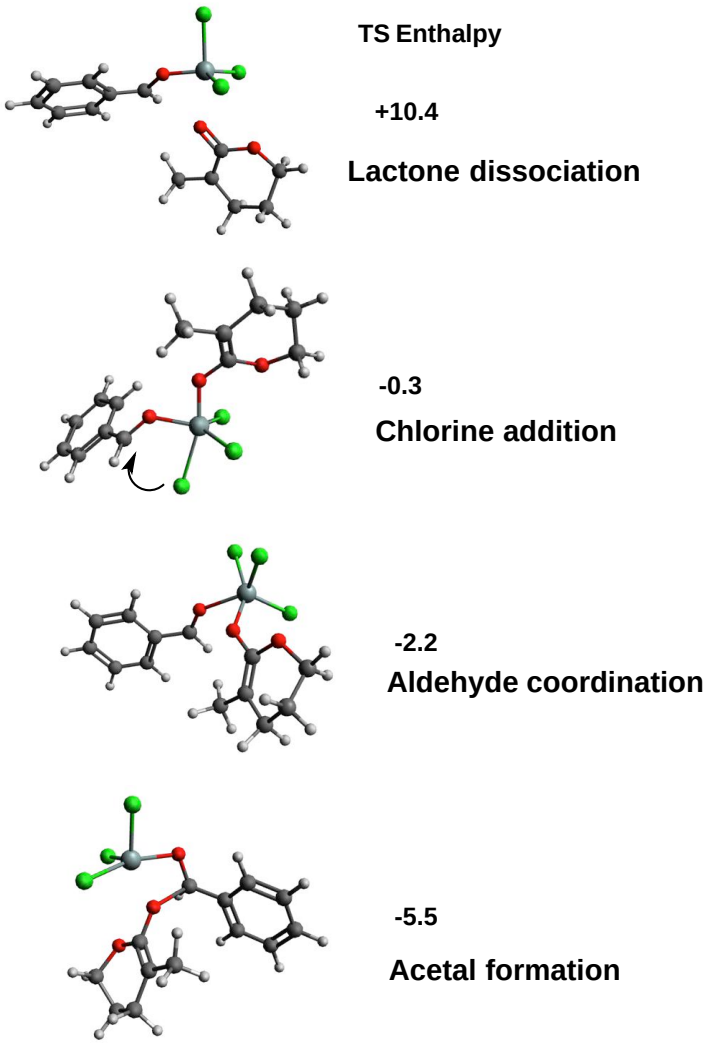



Figure 4.7b Corresponding reaction outcomes found using Zstruct and SMM (Figure 4.7a).

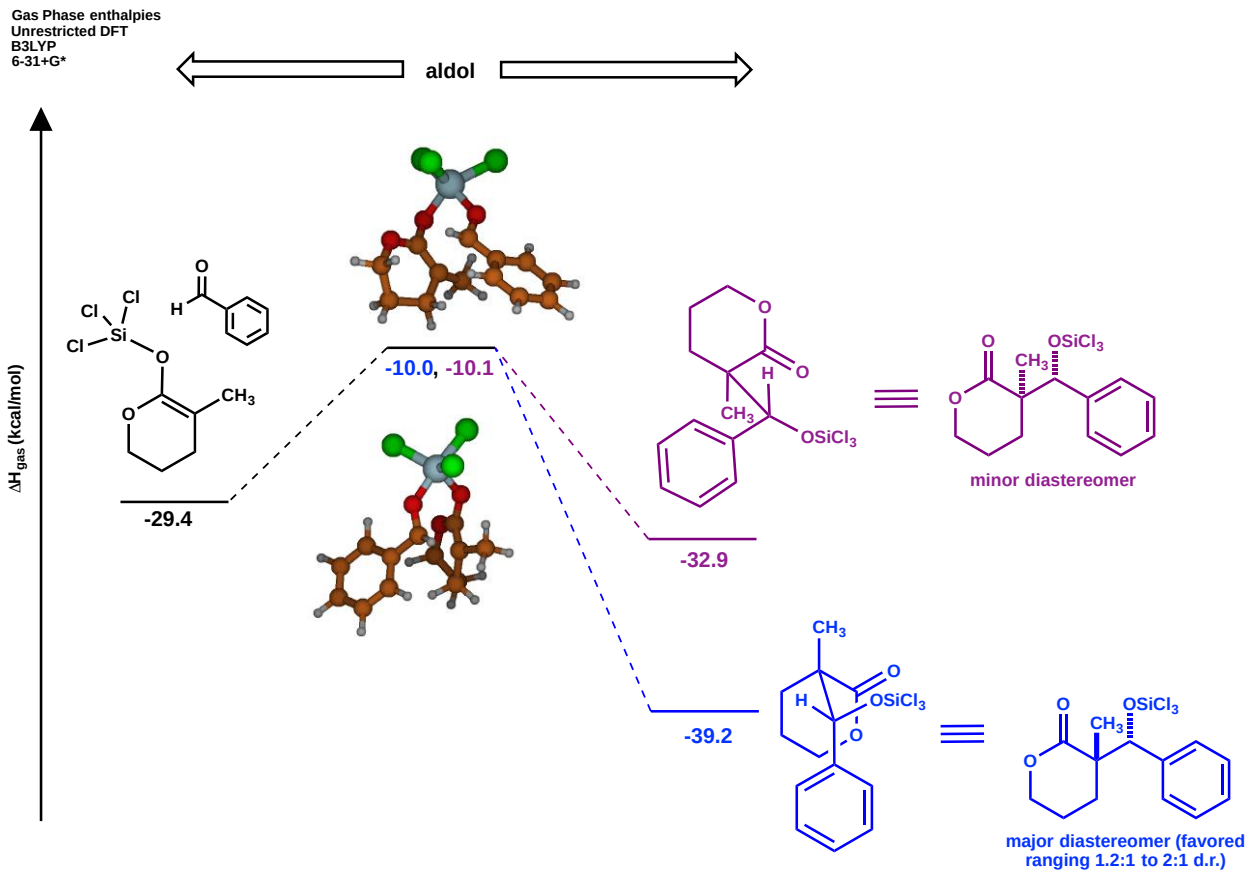
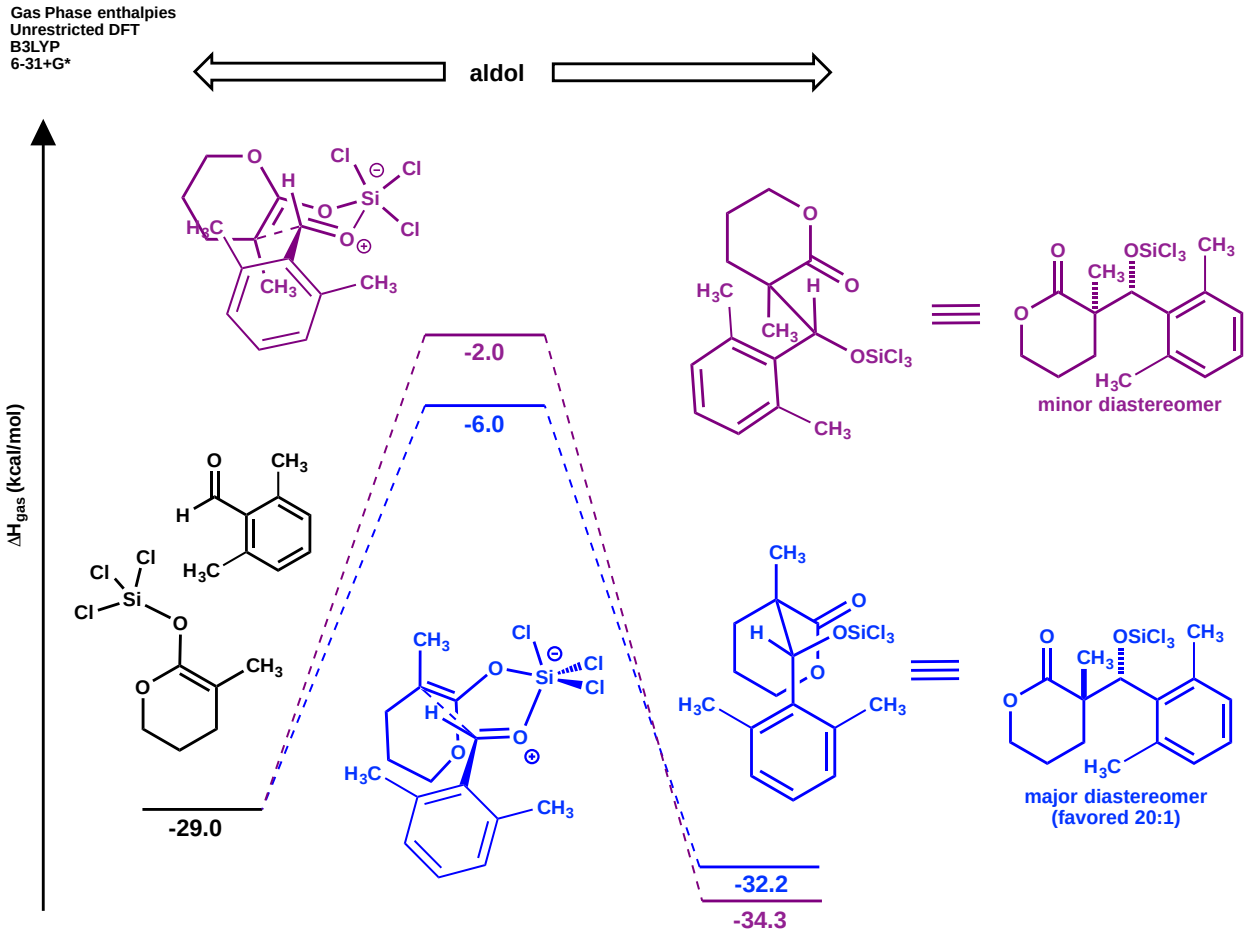



Figure 4.8 Uncatalyzed aldol pathways of the trichlorosilyl enolate and benzaldehyde, leading to two diastereomeric products.

Using Zstruct followed by SSM unfortunately did not reveal the minor diastereomer. Thus, we used a more directed starting structure that positioned the aldehyde in the opposite direction, which worked satisfactorily. Compared to the major product, the transition state energy for the minor product was about the same (-10.1 vs. -10.0 kcal/mol), so these results alone suggest that the catalyst probably plays a role in the aldol step because the d.r. is 2:1. The major diastereomer is formed through a boat-like transition state, with the $–CH_3$ of the enolate and –Ph of PhCHO positioned in opposite directions. The minor diasteromer is a result of a chair TS with the $–CH_3$ of the enolate and –Ph of PhCHO facing the same direction. Comparable transition states were found with the bulkier analog, 2,6-dimethylbenzaldehyde (20:1 d.r.). In this case, the major transition state was noticeably lower in energy than that of the minor product (4 kcal/mol difference), although this does not necessarily endorse an uncatalysed mechanism. The catalyzed TS for both diastereomers were found to be lower in energy (-14.3 and -8.5 kcal/mol, respectively) with a larger gap (5.8 kcal/mol) between products (See Supporting Information).


Gas Phase enthalpies
Unrestricted DFT
B3LYP
6-31+G*
aldol
ΔH gas (kcal/mol)
-2.0
-6.0
-29.0
-32.2
-34.3
minor diastereomer
major diastereomer
(favored 20:1)

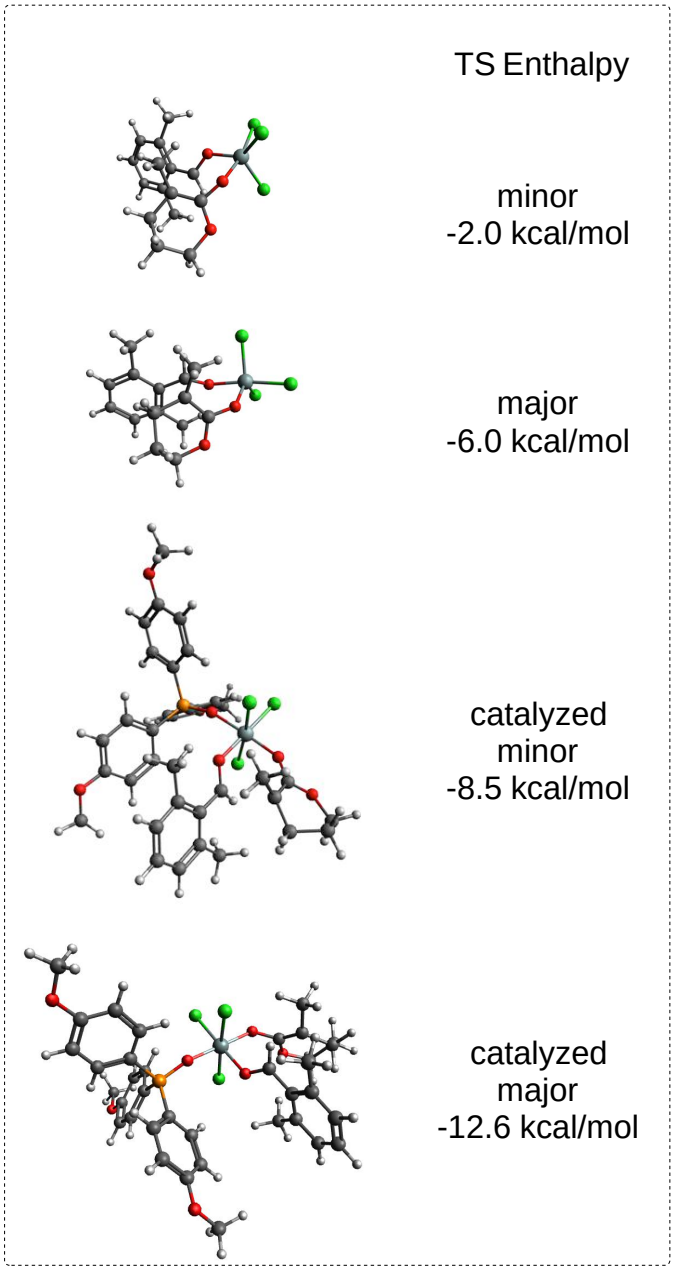



Figure 4.9 Aldol pathways of the trichlorosilyl enolate and 2,6-dimethylbenzaldehyde, leading to two diastereomeric products.

*Catalyzed Aldol and Si-complex geometry*

Because of the lack of energy difference between major and minor products for an uncatalyzed mechanism, we must consider that the catalyst could play a role during the aldol step. It was shown that catalyst dissociation might occur (Figure 4.3, path G), and perhaps the catalyst could re-coordinate in a geometry that encourages the aldol reaction. To get a sense of this equilibrium, we compared the relative energies for different catalysts (Table 4.1) and

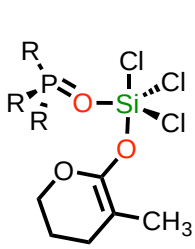
substrates (Table 4.2) at 3 to 4 possible O-Si-O geometries: 90°, 120°, and 180°. For the 90° geometry, two options exist: 1) where the substrate is equatorial and catalyst axial, and 2) the catalyst is equatorial and substrate axial. This difference was overlooked at first, and placement was done arbitrarily before optimization. After closer examination of the output structures, none of the geometries with an equatorial catalyst were the lowest energy structure, but axial catalyst placement gave many lowest energy structures compared to the 120° and 180° variations. Consequently, all structures were positioned with the catalyst axial, and we are waiting for a few more DFT optimizations to be able to compare all relative energies.

Intriguingly, none of the substrates or catalysts favored a 120° geometry as the most stable, although this was the resulting geometry from the reduction (Tables 4.1 & 4.2). Although an 180° geometry logically appears to be most sterically favorable, we hypothesize that this electron-rich catalyst placement weakens the Si-O enolate bond of the lactone. This geometry was only calculated to be most stable for one substrate: I, α-methylene-ε-caprolactone (Table 4.2). All other substrates and catalyst combinations were calculated to be most stable in a 90° conformation with axial catalyst and equatorial substrate placement. Perhaps for α-methylene-ε-caprolactone, increased sterics of a distorted 7-membered ring outweigh electronic bond weakening effects (See Supporting Information for structural details). Although this substrate was calculated to have about the same reduction TS energy as its 6-membered ring equivalent, only 15% yield of aldol product was obtained experimentally. Currently, we are calculating the TS for the aldol step with this substrate to compare relative energies.

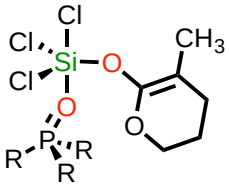
Regardless of which enolate/catalyst geometry is the most favorable for individual substrates, the aldol step could still occur through a different enolate geometry, as the TS energy determines which pathway is energetically favorable, not the energy of the starting structures. Although the 90° conformation was most stable by DFT (Tables 4.1 & 4.2), according to GSM the aldol step TS energy is lowest when the starting structure is positioned in a 180° conformation (-11.3 kcal/mol, Figure 4.10). This is reasonable because this conformation allows open space for the incoming aldehyde, and also the catalyst is positioned directly across from the lactone nucleophile, increasing its nucleophilicity towards the electrophile benzaldehyde. Based on this difference between the most stable (90°) and reactive (180°) species, and also the 120° conformation that results from reduction, we propose that the Si-catalyst-substrate complex might be undergoing fluxional motions such as the Berry Pseudorotation (Figure 4.12). This

hypothesis is an alternative to stepwise catalyst dissociation and re-coordination. The Berry mechanism could allow interchange between isomers without catalyst dissociation, and has been observed for Si complexes before.[106] We will use DE-GSM to find a pathway between the different Si-complex isomers, to see if the Berry mechanism is operative and what its TS energy is compared to the stepwise mechanism.

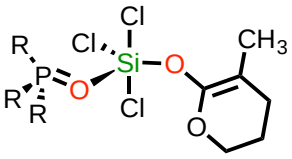
Table 4.1 – A comparison of enolate geometry relative energies for different catalysts



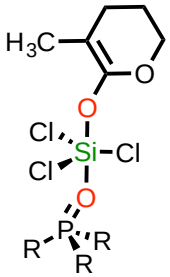

**equitorial 90º**




**axial 90º**




**120º**




**180º**

| | Enolate relative enthalpies in kcal/mol (for each possible **O-Si-O angle**) | | |
|---|---|---|---|
| **Catalyst** | **Axial 90° (DFT angle)** | **120° (DFT angle)** | **180° (DFT angle)** |
| TPPO, R=Ph | n/a | +3.6 (119.9°) | 0 (177.3°) |
| HMPA, R = $NMe_2$ | 0 (84.7°) | +4.5 (119.5°) | +4.7 (177.1°) |
| *p*-OMe-TPPO, R = *p*-OMePh | 0 (82.0°) $\tau_5$= 0.95 | +4.6 (118.1°) $\tau_5$= 0.88 | +2.6 (176.0°) $\tau_5$= 0.91 |
| *o,p*-diOMe-TPPO, R = *o,p*-diOMePh | 0 (83.3°) $\tau_5$= 0.94 | +5.6 (116.7°) $\tau_5$= 0.90 | +9.0 (177.8°) $\tau_5$= 0.90 |
| *p*-$NMe_2$-TPPO R = *p*-$NMe_2$Ph | 0 (88.7°) | +2.0 (118.3°) | +0.8 (177.8°) |
| *o*-OMe-TPPO R = *o*-OMePh | n/a | +2.4 (122.2°) | 0 (175.1°) |

Table 4.2 - A comparison of enolate geometry relative energies for different substrates with the same catalyst *p*-OMeTPPO.

| Enolate relative enthalpies (for each possible **O-Si-O angle**) | | | | |
|---|---|---|---|---|
| Entry | Substrate | **Axial 90° (DFT angle)** | **120° (DFT angle)** | **180° (DFT angle)** |
| 1 | F | 0 (82.0°) | +4.6 (118.1°) | +2.6 (176.0°) |
| 2 | J | 0 (82.1°) | +4.8 (118.5°) | +2.8 (177.2°) |
| 3 | I | +3.1 (88.3°)<br>$\tau_5$= 0.92 | +4.0 (120.1°)<br>$\tau_5$= 0.87 | 0 (177.7°)<br>$\tau_5$= 0.93 |
| 4 | H | n/a | +1.6 (114.2°) | 0 (177.4°) |
| 5 | K | 0 (82.1°) | +3.7 (115.3°) | +2.3 (177.5°) |
| 6 | 7K | 0 (82.2°)<br>$\tau_5$= 0.91 | +5.5 (105.0°)<br>$\tau_5$= 0.68 | +2.3 (176.0°)<br>$\tau_5$= 0.92 |

For most substrates and catalyst combinations, the measured DFT O-Si-O angle did not differ considerably (< 8°) from the approximate angle (90°, 120°, 180°) for a typical trigonal bipyramidal complex. The exception to this trend was the bulkiest substrate, which is a 7-membered ring analogue of the bicyclic substrate K. According to DFT, when both the substrate and catalyst are equatorial after reduction, these substituents are separated by only 105.0° (Table 4.2, entry 6). This complex was calculated to have a geometry index value ($\tau_5$) of 0.68, which was the most distorted structure from a regular trigonal bipyramidal structure $\tau_5$ value of 1. The other isomers of this substrate were considerably less distorted with $\tau_5$ values of 0.91 (90°) and 0.92 (180°). Geometry indices were calculated for a few other catalysts (Table 4.1, *p*-OMe-TPPO and *o,p*-diOMe-TPPO) and substrates (Table 4.2, entry 3), and in all cases, the 120° isomer was most distorted.

*Conclusions and Future Work*

Overall, the lowest energy mechanism we found was consistent with our general hypothesis. Although we did not discover a mechanism that was wholly different from our initial ideas, these calculations revealed geometric details that would be overlooked otherwise. Before these calculations, we were unaware of the different catalyst-Si-enolate geometry isomers. Now that we have enhanced visual ideas of the reduction and aldol transition state structures, more

directed hypotheses can be made for catalyst improvement. Portions of this work will be submitted for publication to *Journal of Organic Chemistry*.

These theoretical investigations can be used to design experimental mechanistic tests. In Chapter III, we did a catalyst screen with benzaldehyde and did not notice any significant change in the diastereomeric ratio. Based on these calculations, that makes sense because for benzaldehyde, energy differences between catalyzed and uncatalyzed for each diastereomer is not significant. A catalyst evaluation with 2-tolualdehyde or 2,6-mesitaldehyde might produce notable differences in d.r. because these substrates are theoretically more stabilized by a suitable catalyst.

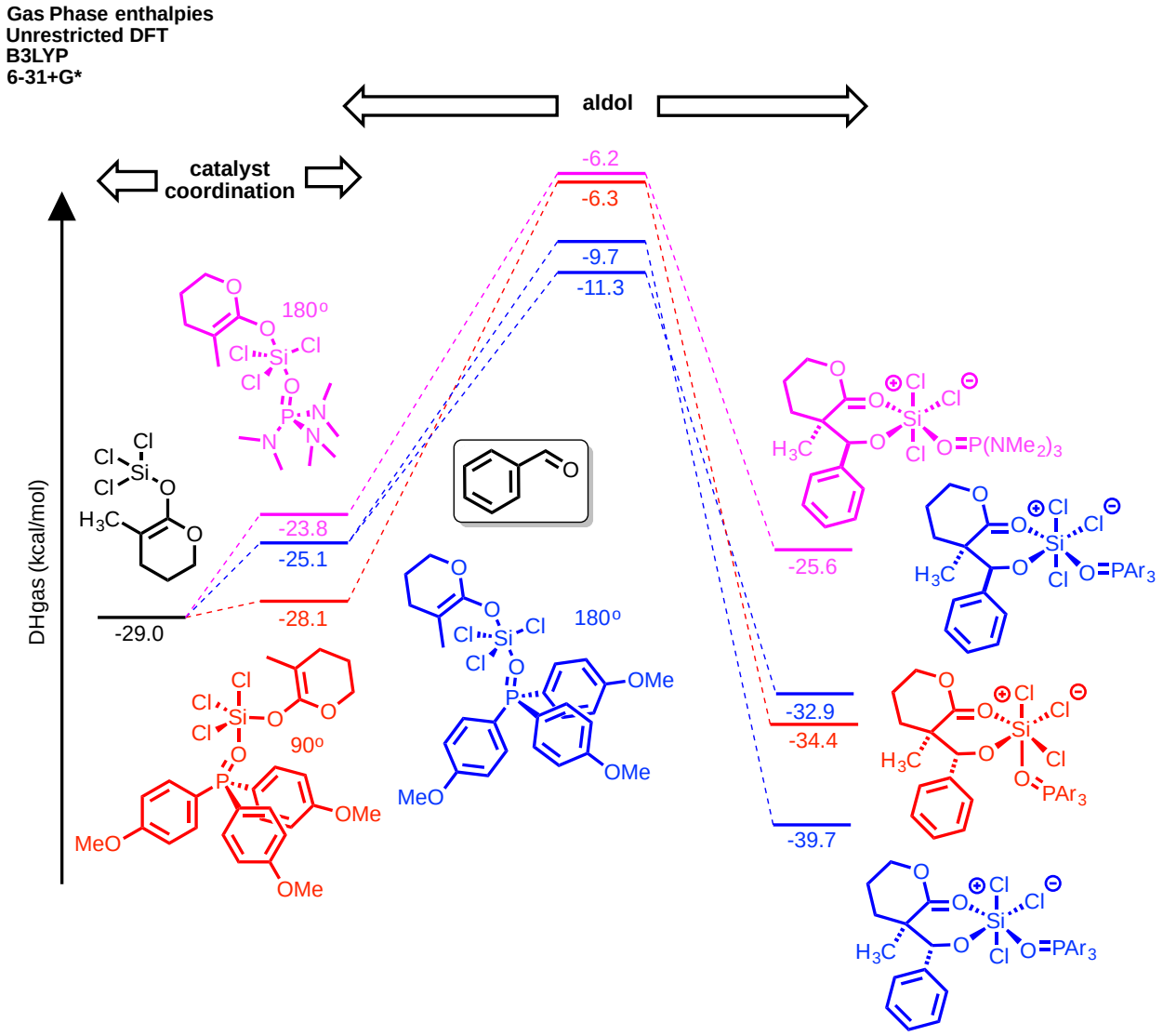



Figure 4.10 Catalyzed aldol simulated in the reverse direction, resulting in 90° (minor product, red) and 180° (major, black & minor, blue) enolate and catalyst geometry.

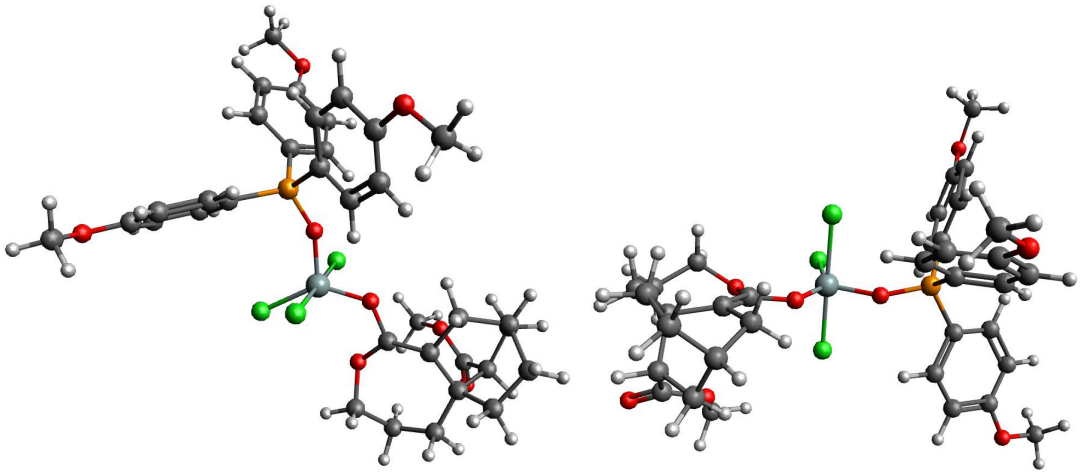


Figure 4.11 – DFT-optimized $\tau_5 \approx 1$ enolate complex of our bulkiest studied substrate with *p*-OMeTPPO catalyst calculated[107] instead to have a geometry index of $\tau_5 = 0.68$.

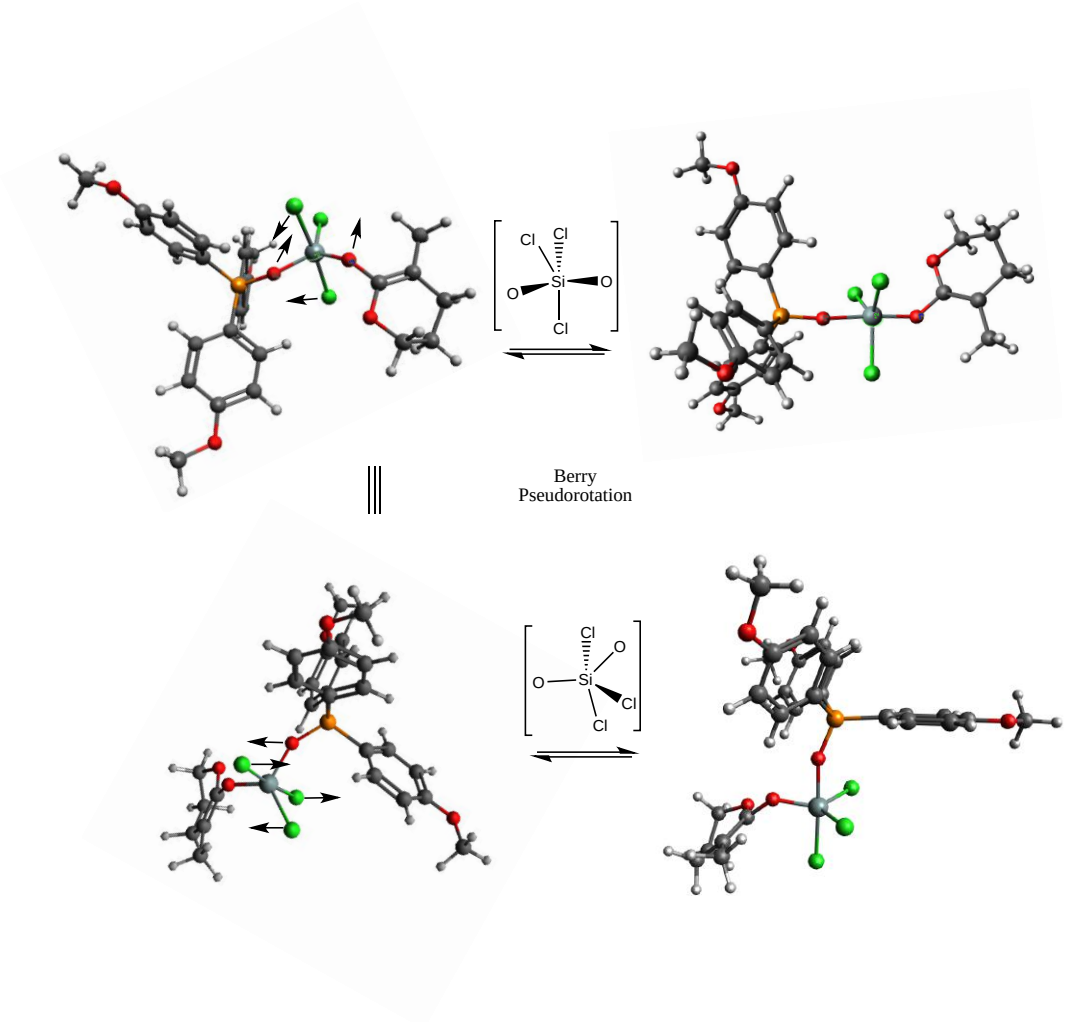



Figure 4.12 – Proposed Berry Pseudo rotation vibration isomer exchange.

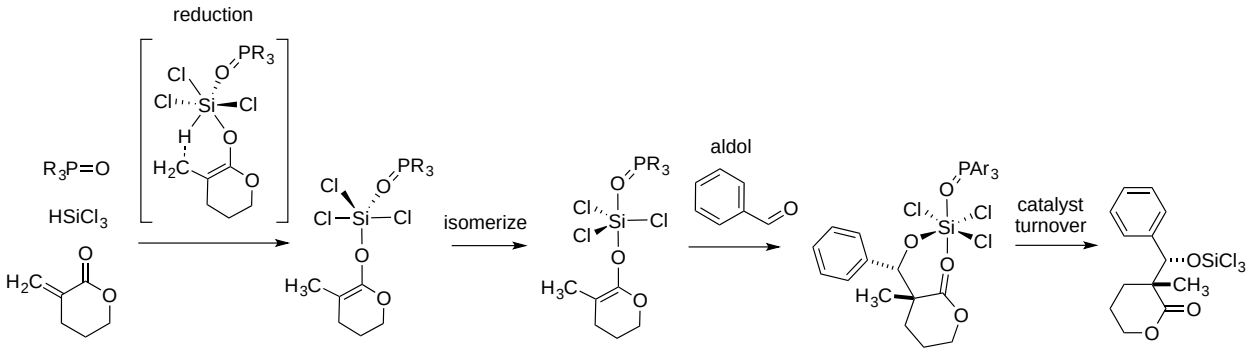
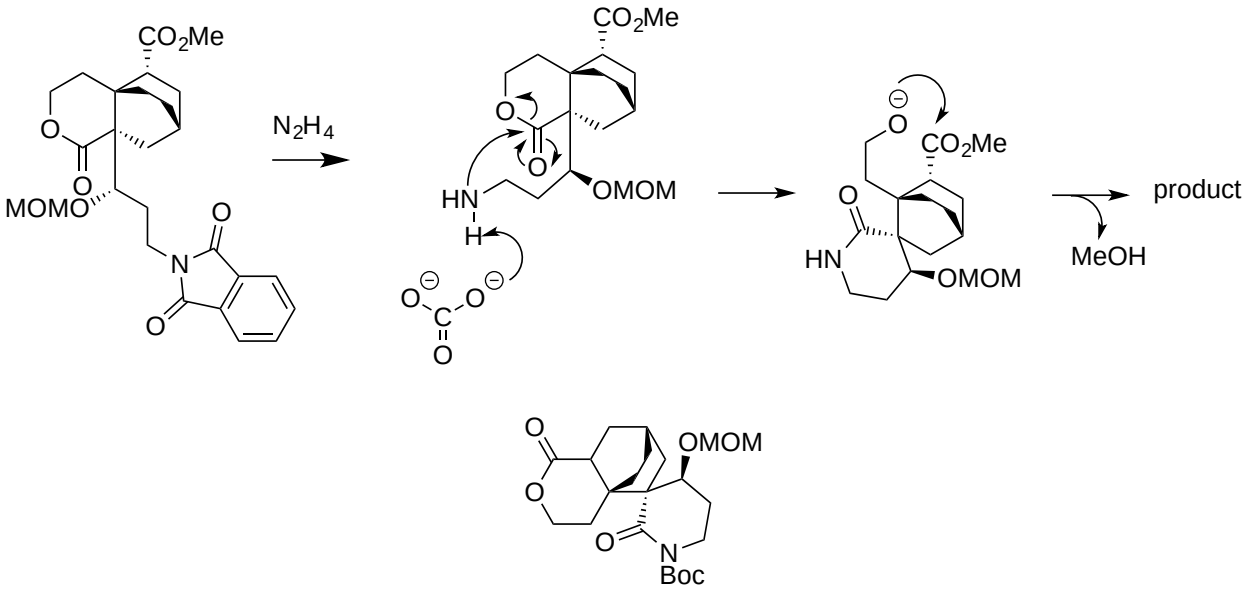


Figure 4.13 Overall Mechanism.

## APPENDIX A: Data and procedures for synthesized compounds



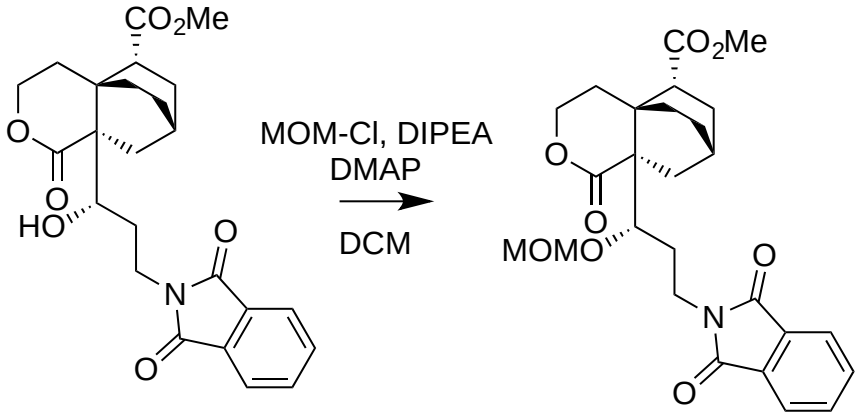

*tert*-butyl (3*S*,4*S*,4a'*R*,7'*R*)-4-(methoxymethoxy)-1',2-dioxohexahydro-1'*H*-spiro[piperidine-3,5'-[4a,7]ethanoisochromene]-1-carboxylate
Chemical Formula: $C_{22}H_{33}NO_7$
Molecular Weight: 423.51

Figure A.1 NPhth deprotection and cyclization/isomerization, followed by Boc protection.

The NPhth compound (0.86 mmol, 419 mg) was dissolved in 5 mL dry EtOH and then $K_2CO_3$ (5 equiv., 4.31 mmol, 596 mg) and $N_2H_4$-$H_2O$ (12 equiv, 10.36 mmol, 645 µL) were added. The solution was heated to reflux for 2 h, and then cooled to ambient temp. Water was added, and then the mixture was extracted with EtOAc, washed with brine, and dried with $Na_2SO_4$. The crude reaction was then Boc-protected. Dissolved in 5 mL dry DCM, triethylamine (3 equiv., 2.58 mmol, 400 µL), DMAP (0.1 equiv., 0.09 mmol, 11 mg), and di-tertbutyl carbonate (3 equiv., 2.58 mmol, 563 mg) were added. The mixture was stirred at ambient temperature for 12 hours and then concentrated under vacuum, purified by Biotage chromatography ($SiO_2$, Ethyl Acetate: Hexanes). The desired product, confirmed by X-ray diffraction as **bocls** (Appendix crystal – a) was the lower isomer by TLC.

$^1$H NMR (400 MHz, $CDCl_3$) δ 4.67 (q, *J* = 7.0 Hz, 2H), 4.19 (m, 1H), 4.10 (m, 1H), 4.04 (m, 1H), 3.70 (m, 1H), 3.58 (m, 1H), 3.39 (s, 3H), 2.42 (m, 2H), 2.08 (m, 2H), 1.81 (d, *J* = 76.9 Hz, 9H), 1.49 (s, 9H), 1.29 (d, *J* = 13.2 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 177.21, 173.80, 154.26, 96.04, 82.65, 80.76, 64.01, 56.76, 51.55, 43.72, 41.39, 41.02, 36.92, 32.77, 31.71, 27.95, 27.15, 24.85, 24.73, 23.18. HRMS (ESI+): calculated for $C_{22}H_{33}NO_7$ $[M+H]^+$: 424.2330, found:

424.2328; calculated for $C_{22}H_{33}NO_7$ $[M+Na]^+$: 446.2149, found: 446.2144. FT-IR ($cm^{-1}$): 1719.5, 1687.2, 1279.7, 1152.5, 1138.9, 1125.1, 1106.9, 1098.1, 1025.4.

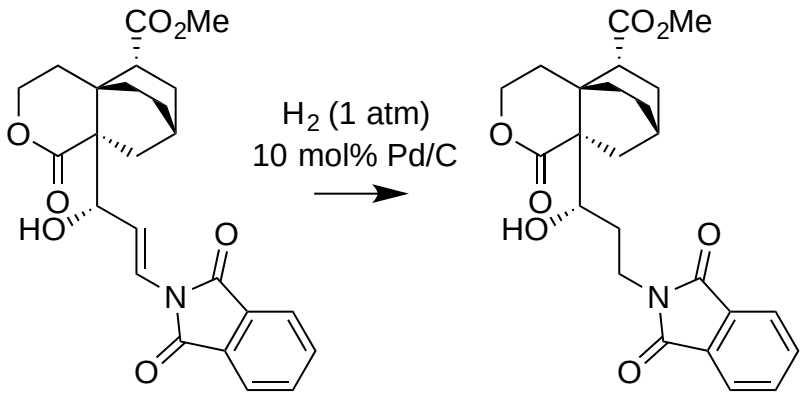



methyl (4a*R*,5*R*,7*R*,8a*S*)-8a-((*S*)-3-(1,3-dioxoisoindolin-2-yl)-1-(methoxymethoxy)propyl)-1-oxooctahydro-4a,7-ethanoisochromene-5-carboxylate
Chemical Formula: $C_{26}H_{31}NO_8$
Molecular Weight: 485.53

Figure A.2 MOM-protection of hydrogenated reductive aldol product.

The alcohol (1.37 mmol, 606 mg), distilled DIPEA (8 equiv, 10.96 mmol, 2 mL), and DMAP (35 mol%, 0.5 mmol, 60 mg) were dissolved in a 45 mL pressure tube with 10 mL DCM, and lastly MOM-Cl (8 equiv., 10.96 mmol, 830 uL) was added drop wise under nitrogen gas at 0°C using an upside down septa as a temporary cap for the pressure tube. After removing the ice bath and stirring for 10 minutes at ambient temperature, the pressure tube was tightly sealed and the mixture was slightly heated using a heating block or oil bath at 45°C for 48 h. The reaction was cooled to ambient temp, and then added 10 mL of saturated $NaHCO_3$ solution. An aqueous extraction with DCM, drying with $Na_2SO_4$, followed by column chromatography ($SiO_2$, Ethyl Acetate: Hexanes) gave 90% yield of the white solid.

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 2H), 7.73 – 7.68 (m, 2H), 4.81 (s, 2H), 4.46 (td, *J* = 10.5, 4.8 Hz, 1H), 4.21 (tt, *J* = 11.5, 5.8 Hz, 1H), 3.98 (ddd, *J* = 14.9, 8.8, 6.3 Hz, 1H), 3.86 – 3.77 (m, 2H), 3.65 (s, 3H), 3.40 (s, 3H), 2.52 (dt, *J* = 15.5, 7.7 Hz, 1H), 2.43 (dd, *J* = 11.4, 4.2 Hz, 1H), 2.30 (d, *J* = 14.4 Hz, 1H), 2.12 (ddd, *J* = 12.9, 10.3, 5.6 Hz, 1H), 2.01 (ddd, *J* = 13.1, 8.8, 3.6 Hz, 2H), 1.82 – 1.47 (m, 9H), 1.46 – 1.40 (m, 1H), 1.31 – 1.22 (m, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 175.34, 173.93, 168.38, 133.92, 132.11, 123.13, 96.56, 83.10, 66.65, 56.43, 52.22, 51.81, 47.80, 37.19, 37.06, 33.68, 31.93, 31.50, 30.60, 29.64, 24.85, 24.63. HRMS (ESI+): calculated for $C_{26}H_{31}NO_8$ $[M+H]^+$: 486.2122, found: 486.2126; calculated for $C_{26}H_{31}NO_8$ $[M+NH_4]^+$: 503.2388, found: 503.2386. IR ($cm^{-1}$): 1708.8, 1373.0, 1226.7, 1177.3, 1136.1, 1069.3, 1028.9, 719.9.

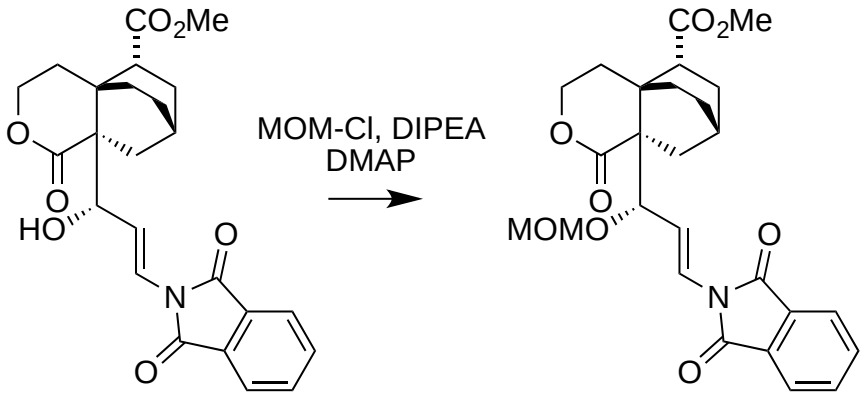



methyl (4a*R*,5*R*,7*R*,8a*S*)-8a-((*S*)-3-(1,3-dioxoisoindolin-2-yl)-1-hydroxypropyl)-1-oxooctahydro-4a,7-ethanoisochromene-5-carboxylate
Chemical Formula: $C_{24}H_{27}NO_7$
Molecular Weight: 441.48

Figure A.3 Hydrogenation of reductive aldol product.

The alkene was hydrogenated with 10 mol% Pd/C with an $H_2$ balloon with THF as a solvent in 12 hours. The desired product was confirmed by X-ray diffraction as **ydraph2** (Appendix crystal – b).

TLC: 0.34 in 7:3 (EtOAc: Hexanes). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 4.8, 3.2 Hz, 2H), 7.73 (dd, *J* = 5.2, 3.0 Hz, 2H), 5.29 (s, 1H), 4.54 (td, *J* = 10.5, 4.2 Hz, 1H), 4.18 (dt, *J* = 14.8, 8.9 Hz, 1H), 3.91 – 3.77 (m, 2H), 3.69 (dt, *J* = 13.4, 6.6 Hz, 1H), 3.64 (s, 3H), 3.33 (d, *J* = 5.9 Hz, 1H), 2.49 (ddd, *J* = 13.1, 10.0, 6.7 Hz, 1H), 2.42 (dd, *J* = 11.5, 4.1 Hz, 1H), 2.27 (dd, *J* = 19.2, 12.4 Hz, 2H), 2.06 – 1.21 (m, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 175.73, 174.14, 168.95, 134.25, 131.77, 123.45, 74.88, 66.98, 51.78, 51.74, 48.06, 37.02, 35.07, 33.78, 32.08, 31.69, 30.80, 30.00, 25.13, 24.60. IR ($cm^{-1}$): 3416, 2940, 1769, 1732, 1701, 1436, 1397, 1370, 1230, 1170, 1130, 1039, 958, 924, 866, 797, 720. HRMS (ESI+): calculated for $C_{24}H_{27}NO_7$ $[M+H]^+$: 442.186, found: 442.1851; calculated for $C_{24}H_{27}NO_7$ $[M+Na]^+$: 464.168, found: 464.1672.

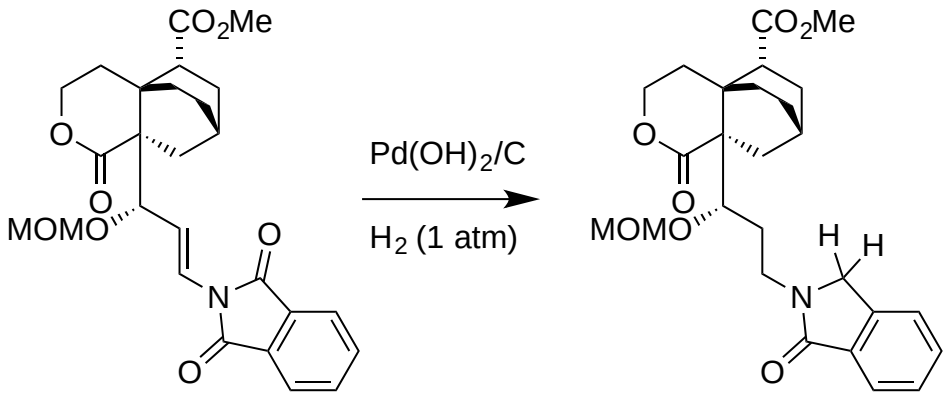



methyl (4a*R*,5*R*,7*R*,8a*S*)-8a-((*S*,*E*)-3-(1,3-dioxoisoindolin-2-yl)-1-(methoxymethoxy)allyl)-1-oxooctahydro-4a,7-ethanoisochromene-5-carboxylate
Chemical Formula: $C_{26}H_{29}NO_8$
Molecular Weight: 483.52

Figure A.4 MOM protection of reductive aldol product.

The same MOM-protection technique was used for this alkene and the hydrogenated analog. The alcohol (1.37 mmol, 606 mg), distilled DIPEA (8 equiv, 10.96 mmol, 2 mL), and DMAP (35 mol%, 0.5 mmol, 60 mg) were dissolved in a 45 mL pressure tube with 10 mL DCM, and lastly MOM-Cl (8 equiv., 10.96 mmol, 830 uL) was added drop wise at 0°C with an upside down septa. After warming to ambient temperature, the pressure tube was tightly sealed and the mixture was heated at 45°C for 48 h. The reaction was cooled to ambient temp, and then added saturated $NaHCO_3$ to quench. An aqueous extraction with DCM, drying with $Na_2SO_4$, followed by column chromatography gave 86% yield.

$^1$H NMR (700 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.75 (dd, *J* = 5.4, 3.0 Hz, 2H), 6.80 (d, *J* = 14.8 Hz, 1H), 6.57 (dd, *J* = 14.8, 9.7 Hz, 1H), 4.78 (d, *J* = 6.8 Hz, 1H), 4.53 – 4.46 (m, 2H), 4.39 (d, *J* = 9.7 Hz, 1H), 4.29 (td, *J* = 10.2, 6.8 Hz, 1H), 3.66 (s, 3H), 3.40 (s, 3H), 2.50 (dd, *J* = 11.4, 4.1 Hz, 1H), 2.37 (ddd, *J* = 12.9, 10.4, 6.8 Hz, 1H), 2.23 (d, *J* = 14.4 Hz, 1H), 1.99 (dd, *J* = 35.2, 25.5 Hz, 3H), 1.85 (s, 2H), 1.69 (s, 1H), 1.61 (s, 2H), 1.52 (d, *J* = 32.4 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 1H).$^{13}$C NMR (176 MHz, $CDCl_3$) δ 175.47, 173.53, 165.99, 134.56, 131.51, 123.72, 123.32, 116.37, 93.55, 81.88, 66.64, 56.83, 51.96, 51.72, 47.42, 37.08, 33.27, 31.84, 30.55, 29.78, 24.97, 24.47. HRMS (ESI+): calculated for $C_{26}H_{29}NO_8$ $[M+NH_4]^+$: 501.2233, found: 501.2234. FT-IR ($cm^{-1}$): 1718.3, 1385.8, 1178.3, 1136.5, 1063.9, 1010.3, 955.2.

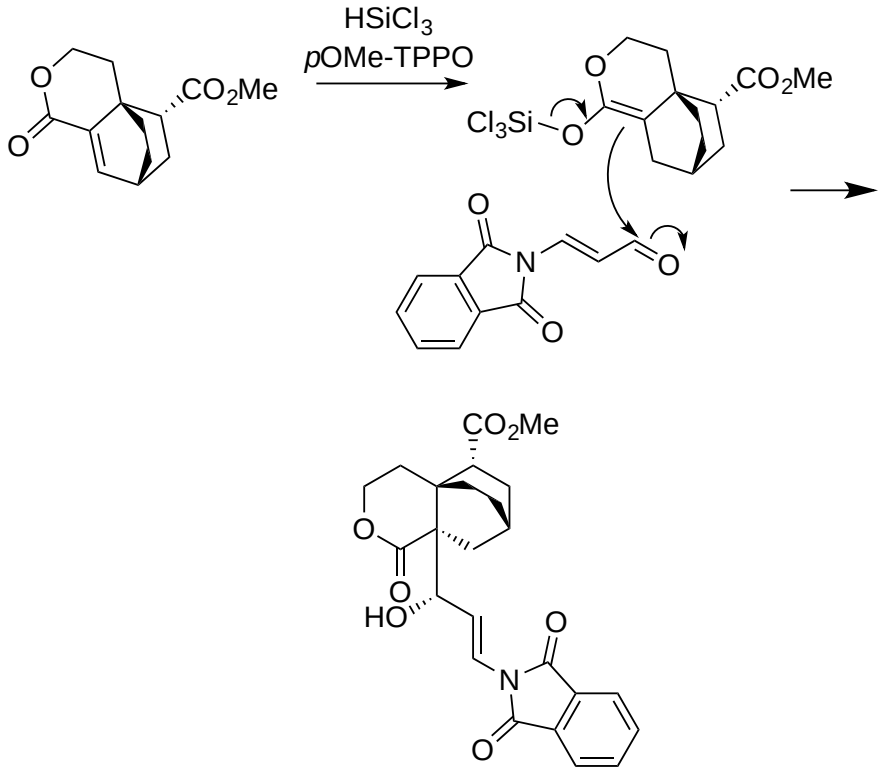



methyl (4a*R*,5*R*,7*R*,8a*S*)-8a-((*S*)-1-(methoxymethoxy)-3-(1-oxoisoindolin-2-yl)propyl)-1-oxooctahydro-4a,7-ethanoisochromene-5-carboxylate
Chemical Formula: $C_{26}H_{33}NO_7$
Molecular Weight: 471.55

Figure A.5 Over-reduction amide side product from hydrogenating MOM-protected reductive aldol product.

Alkene was hydrogenated with 10 mol% $Pd(OH)_2/C$ with a $H_2$ balloon in THF as a solvent overnight. This over-reduction lactam product was isolated in 13% yield in addition to the NPhth product in 48% yield. This route was not pursued further because of the over-reduction issue. It is easier to hydrogenate the product before alcohol protection instead.

$^1$H NMR (700 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 2H), 4.96 (d, *J* = 6.6 Hz, 1H), 4.81 (d, *J* = 6.6 Hz, 1H), 4.54 – 4.46 (m, 2H), 4.34 (d, *J* = 16.9 Hz, 1H), 4.22 (td, *J* = 10.4, 5.3 Hz, 1H), 4.16 – 4.09 (m, 1H), 3.87 (dd, *J* = 5.4, 2.4 Hz, 1H), 3.66 (s, 3H), 3.54 – 3.48 (m, 1H), 3.41 (s, 3H), 2.51 – 2.44 (m, 1H), 2.41 (dd, *J* = 11.4, 4.2 Hz, 1H), 2.25 (d, *J* = 14.1 Hz, 1H), 2.16 (ddd, *J* = 13.1, 10.3, 5.3 Hz, 1H), 2.03 – 1.99 (m, 1H), 1.95 (d, *J* = 13.3 Hz, 1H), 1.73 (dd, *J* = 84.3, 27.4 Hz, 5H), 1.58 (dd, *J* = 13.4, 11.4 Hz, 1H), 1.47 (dd, *J* = 18.0, 11.2 Hz, 3H), 1.22 – 1.17 (m, 1H). $^{13}$C NMR (176 MHz, $CDCl_3$) δ 175.41, 174.51, 168.86, 141.13, 132.65, 131.30, 128.04, 123.50, 122.75, 97.25, 83.54, 66.78, 56.35, 52.16, 51.82, 50.00, 47.68, 40.95, 36.94, 33.87, 31.69, 31.42, 30.57, 29.64, 24.72, 24.63.




methyl (4a*R*,5*R*,7*R*,8a*S*)-8a-((*S*,*E*)-3-(1,3-dioxoisoindolin-2-yl)-1-hydroxyallyl)-1-oxooctahydro-4a,7-ethanoisochromene-5-carboxylate

Chemical Formula: $C_{24}H_{25}NO_7$

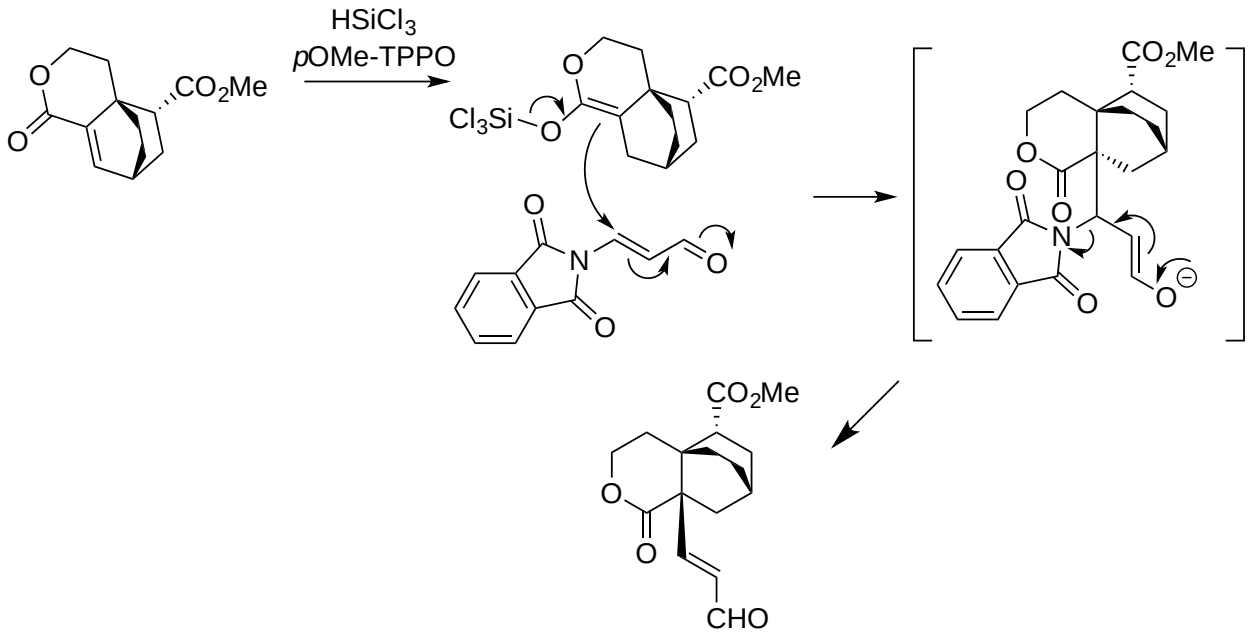
Molecular Weight: 439.46

Figure A.6 Reductive aldol towards isopalhinine.

The bicyclic core (3.85 mmol, 910 mg) and the catalyst (20 mol%, 0.77 mmol, 284 mg) were combined in a flame-dried 50 mL round bottom flask, and 16 mL of dry DCM was added under nitrogen. At 0°C, neat trichlorosilane was added dropwise (1.2 equiv., 4.62 mmol, 470 uL), and the solution was allowed to reach ambient temperature. Upon consumption of the alkene after about 4-8 hours ($R_f$ of staring material and reduced intermediate both approximately 0.25 in 50% EtOAc:Hexanes, but $KMnO_4$ stain can indicate when the starting material is mostly consumed), a solution of aldehyde (1.2 equiv., 4.24 mmol, 853 mg) in DCM (15 mL) was added at 0°C, dropwise and then left to stir overnight. To quench the reaction, it was diluted with Ethyl Acetate, and then a few drops of saturated $NaHCO_3$ were added dropwise, with stirring, until the development of gas ceased. To the mixture was added $Na_2SO_4$, with stirring, and was filtered over celite. Column chromatography was used with a gradient from 30/40% → 100% Ethyl Acetate in Hexanes. The reaction mixture must be loaded in solution, and it is best to not fully evaporate the reaction mixture, as it can be difficult to re-dissolve. If it is loaded as a solid, the product will be very streaky and will require flushing with MeOH to fully elute. TLC: 0.29 in 7:3 (EtOAc: Hexanes) Stain: CAM (blue) or anisaldehyde (green). The desired product was confirmed by X-ray diffraction as **ydrap** (Appendix crystal – c).

TLC: 0.29 in 7:3 (EtOAc: Hexanes) $^1$H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.0 Hz, 2H), 6.90 – 6.86 (m, 2H), 4.57 – 4.44 (m, 2H), 4.27 (ddd, *J* =

11.3, 9.1, 7.9 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 1H), 3.67 (s, 3H), 2.50 (ddd, *J* = 13.3, 10.7, 5.8 Hz, 2H), 2.25 (d, *J* = 14.3 Hz, 1H), 2.06 – 1.49 (m, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 175.80, 173.80, 166.04, 134.58, 131.52, 123.77, 122.04, 119.78, 78.57, 66.99, 51.68, 48.14, 36.99, 33.48, 32.13, 30.69, 30.10, 25.08, 24.54. IR ($cm^{-1}$): 3453, 2924, 1713, 1376, 1165, 1140, 1071, 1018, 955, 726. HRMS (ESI+): calculated for $C_{24}H_{25}NO_7$ $[M+H]^+$: 440.1704, found: 440.1700, calculated for $C_{24}H_{25}NO_7$ $[M+NH_4]^+$: 457.1969, found: 457.1971; calculated for $C_{24}H_{25}NO_7$ $[M+Na]^+$: 462.1523, found: 462.1520.




methyl (4a*R*,5*R*,7*R*,8a*R*)-1-oxo-8a-((*E*)-3-oxoprop-1-en-1-yl)octahydro-4a,7-ethanoisochromene-5-carboxylate

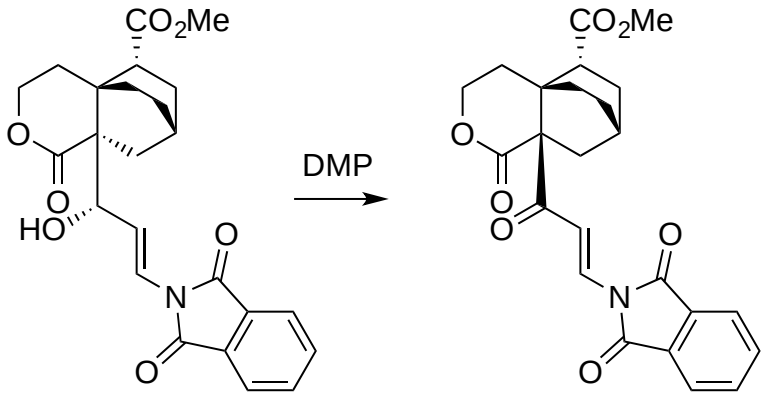
Chemical Formula: $C_{16}H_{20}O_5$

Molecular Weight: 292.33

Figure A.7 Reductive aldol side product (1,4-addition to aldehyde).

This was isolated as a side product in 15% yield while conducting the previous reductive aldol procedure on a 1g scale, in some reactions depending on the variability of reagents.

$^1$H NMR (500 MHz, $CDCl_3$) δ 9.55 (d, *J* = 7.1 Hz, 1H), 7.03 (d, *J* = 16.0 Hz, 1H), 6.20 (dd, *J* = 16.0, 7.1 Hz, 1H), 4.22 (m, 2H), 3.68 (s, 3H), 2.69 (d, *J* = 14.4 Hz, 1H), 2.58 (dd, *J* = 11.1, 3.6 Hz, 1H), 2.12 – 1.51 (m, 10H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 192.60, 175.17, 172.09, 156.81, 132.50, 65.37, 51.92, 48.78, 48.19, 36.49, 35.51, 32.23, 29.78, 29.47, 24.45, 24.32. HRMS (ESI+): calculated for $C_{16}H_{20}O_5$ $[M+H]^+$: 239.1384, found: 293.1390; calculated for $C_{16}H_{20}O_5$ $[M+NH_4]^+$: 310.1649, found: 310.1652. FT-IR ($cm^{-1}$): 1727.8, 1683.0, 1222.9, 1206.8, 1174.1, 1135.8, 1103.0, 1071.5, 1021.8, 983.8, 926.0.

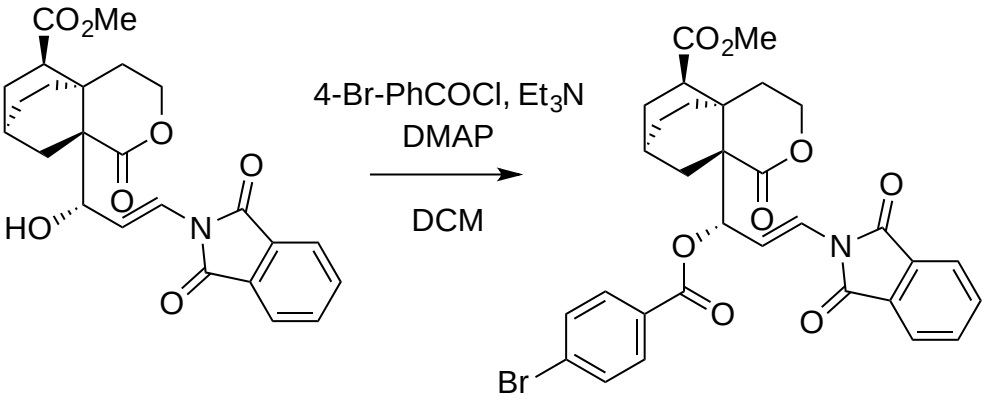



methyl (4a*R*,5*R*,7*R*,8a*S*)-8a-((*E*)-3-(1,3-dioxoisoindolin-2-yl)acryloyl)-1-oxooctahydro-4a,7-ethanoisochromene-5-carboxylate
Chemical Formula: $C_{24}H_{23}NO_7$
Molecular Weight: 437.45

Figure A.8 Oxidation of reductive aldol product.

The alcohol (30 mg, 0.07 mmol) of was dissolved in 3 mL of DCM, and added 1.2 equiv. of DMP reagent (0.08 mmol, 35 mg). The mixture was stirred overnight, and quenched with saturated $NaHCO_3$ in water, extracted with EtOAc, washed with brine, and purified by column chromatography (EtOAc in Hexanes) to yield the ketone.

$^1$H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.91 (m, 3H), 7.82 (dt, *J* = 5.8, 2.9 Hz, 2H), 7.64 (dd, *J* = 14.3, 2.9 Hz, 1H), 4.27 (tt, *J* = 9.3, 3.2 Hz, 1H), 4.20 – 4.07 (m, 1H), 3.70 (d, *J* = 2.9 Hz, 3H), 2.89 (dd, *J* = 14.3, 2.5 Hz, 1H), 2.44 (dd, *J* = 23.5, 20.0 Hz, 3H), 2.34 – 2.23 (m, 1H), 2.11 (d, *J* = 16.9 Hz, 2H), 1.98 (d, *J* = 2.1 Hz, 1H), 1.72 (ddd, *J* = 13.7, 11.2, 2.7 Hz, 1H), 1.64 – 1.43 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 194.78, 174.42, 171.09, 165.24, 135.27, 131.35, 131.11, 124.33, 111.52, 65.71, 59.12, 51.92, 50.76, 36.31, 34.34, 33.85, 33.82, 31.97, 29.18, 28.84, 25.18, 24.69. HRMS (ESI+): calculated for $C_{24}H_{23}NO_7$ $[M+H]^+$: 438.1547, found: 438.1548. FT-IR ($cm^{-1}$): 1725.5, 1689.0, 1612.8, 1599.6, 1381.9, 1317.5, 1194.3, 1121.0, 1017.2, 717.4.




methyl (4a*R*,5*R*,7*R*,8a*S*)-8a-((*S*,*E*)-1-((4-bromobenzoyl)oxy)-3-(1,3-dioxoisoindolin-2-yl)allyl)-1-oxooctahydro-4a,7-ethanoisochromene-5-carboxylate

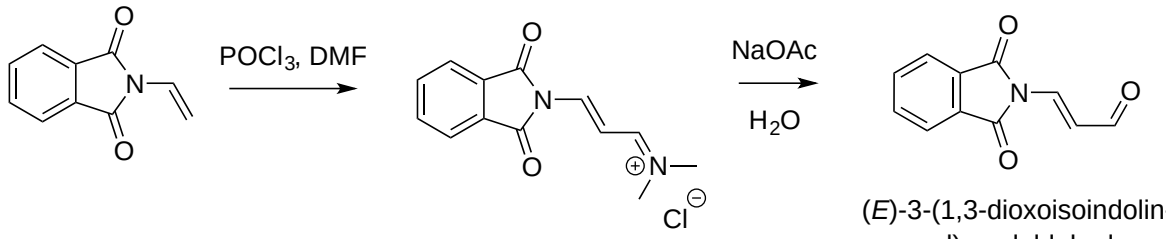
Chemical Formula: $C_{31}H_{28}BrNO_8$

Molecular Weight: 622.47

Figure A.9 Ester protection of reductive aldol product.

The reductive aldol product alcohol (30 mg, 0.07 mmol) was dissolved in 5 mL of DCM and added $Et_3N$ (1.5 equiv., 0.10 mmol, 10 mg, 14 µL), *p*-bromobenzoyl chloride (1.5 equiv., 0.10 mmol, 22 mg), and DMAP (20 mol%, 0.02 mmol, 3 mg) at 0 °C, and allowed to warm to r.t. and stirred overnight. Water was added, and then extracted with EtOAc, washed with Brine, and purified by flash chromatography (EtOAc and Hexanes)

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.86 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.73 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 14.7 Hz, 1H), 6.92 (dd, *J* = 14.7, 9.3 Hz, 1H), 5.99 (d, *J* = 9.4 Hz, 1H), 4.40 – 4.24 (m, 2H), 3.70 (s, 3H), 2.54 (dd, *J* = 11.3, 3.2 Hz, 1H), 2.38 (d, *J* = 14.9 Hz, 1H), 1.97 – 1.47 (m, 10H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 175.78, 172.26, 165.84, 164.17, 134.62, 132.01, 131.44, 131.17, 128.90, 128.40, 124.43, 123.76, 114.70, 78.66, 66.42, 51.80, 51.09, 46.65, 36.89, 32.96, 32.20, 30.27, 24.67, 24.45, 14.18. HRMS (ESI+): calculated for $C_{31}H_{28}BrNO_8$ $[M+NH_4]^+$: 639.1337, found: 639.1335. FT-IR ($cm^{-1}$): 1723.1, 1707.3, 1381.0, 1260.8, 1221.8, 1067.7, 760.9, 717.0.



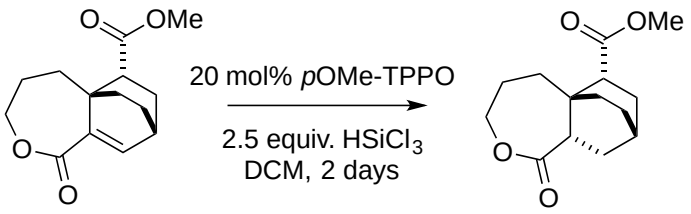

(*E*)-3-(1,3-dioxoisoindolin-2-yl)acrylaldehyde
Chemical Formula: $C_{11}H_7NO_3$
Molecular Weight: 201.18

Figure A.10 Literature-reported synthesis of N-containing aldehyde.

Main Procedure: Yanagi, K.; Nishiyama, T. *Nippon Kagaku Kaishi,* 1978, *3,* 404-11.
Procedure for making the Vilsmeier reagent: Schmidle, C. J.; Barnett, P. G. *J. Am. Chem. Soc*., 1956, *78*, 3209–3210.

To a stirred solution of DMF (13 mL) in a round bottom flask under Nitrogen in an ice bath was added dropwise 2.4 mL of $POCl_3$ (25.4 mmol), keeping the temperature below 20°C. A solution of N-vinyl imide (3.36g, 19.4 mmol) dissolved in DMF (13 mL) was then added to the Vilsmeier reagent prepared at room temperature. The reaction was slowly heated to 65°C and stirred for 2 hours at this temperature. The reaction was cooled to room temperature and then chilled in an ice bath for an hour to precipitate out the iminium salt. The precipitate was collected by vacuum filtration and washed with chloroform 2-3 times. The iminium salt was then dried under vaccum. In a round bottom flask was combined 560 mg of iminium salt (2.12 mmol), 18 mg NaOAc (0.22 mmol), and 3 mL of H2O. This mixture was heated to 50°C for 1 hour. Reaction was cooled down to room temperature, then collected solids by vacuum filtration. Material can either be recrystallized from ethanol or purified by column chromatography.

TLC: $R_f$ = 0.28 in 3:7 (EtOAc: Hexanes) $^1$H NMR (500 MHz, $CDCl_3$) δ 9.61 (d, *J* = 7.9 Hz, 1H), 7.99 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.86 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.71 (d, *J* = 14.8 Hz, 1H), 7.21 (dd, *J* = 14.8, 7.9 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 192.89, 164.94, 137.99, 135.51, 131.33, 124.53, 118.82. IR ($cm^{-1}$): 3090.2, 3058.7, 2846.5, 1786.3, 1727.5, 1676.2, 1629.7, 1463.5, 1365.2, 1309.1, 1139.9, 1065.6, 977.0, 716.11. HRMS (ESI+): calculated for $C_{11}H_7NO_3$ $[M+H]^+$: 202.0499, found: 202.0501; calculated for $C_{11}H_7NO_3$ $[M+Na]^+$: 224.0318, found: 224.0320.

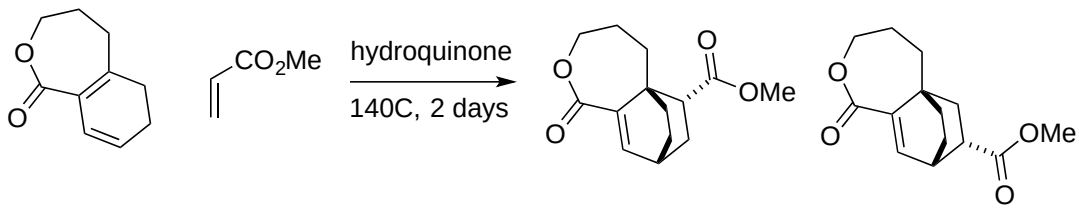



methyl (5a*R*,6*R*,8*R*,9a*S*)-1-oxooctahydro-3*H*-5a,8-ethanobenzo[*c*]oxepine-6-carboxylate
Chemical Formula: $C_{14}H_{20}O_4$
Molecular Weight: 252.31

Figure A.11 Reduction of 7-membered ring lactone core.

The bicyclic core (50 mg, 0.2 mmol) and the *p*OMe-TPPO catalyst (20 mol%, 0.04 mmol, 15 mg) were combined in a flame-dried 10 mL round bottom flask, and 4 mL of dry DCM was added under nitrogen. At 0°C, neat trichlorosilane was added dropwise (2 equiv., 0.4 mmol, 40 µL), and the solution was allowed to reach ambient temperature. Alkene was consumed after about 48 hours ($R_f$ of staring material and reduced intermediate both approximately 0.25 in 50% EtOAc:Hexanes, but $KMnO_4$ stain can indicate when the starting material is mostly consumed) To quench the reaction, it was diluted with Ethyl Acetate, and then a few drops of saturated $NaHCO_3$ were added dropwise, with stirring, until the development of gas ceased. To the mixture was added $Na_2SO_4$, with stirring, and was filtered over celite. Column chromatography was used with Ethyl Acetate in Hexanes.

$^1$H NMR (500 MHz, $CDCl_3$) δ 4.24 (dt, *J* = 12.6, 4.1 Hz, 1H), 4.18 – 4.10 (m, 1H), 3.66 (s, 3H), 2.69 (dd, *J* = 10.2, 3.7 Hz, 1H), 2.63 (d, *J* = 13.5 Hz, 1H), 2.37 (t, *J* = 9.4 Hz, 1H), 2.14 – 2.00 (m, 2H), 1.74 (qd, *J* = 9.6, 5.2 Hz, 3H), 1.57 (dt, *J* = 18.3, 11.6 Hz, 5H), 1.49 – 1.37 (m, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 175.41, 174.86, 67.24, 51.54, 46.18, 41.88, 37.53, 37.14, 35.60, 28.69, 27.84, 25.19, 24.59, 23.32. HRMS (ESI+): calculated for $C_{14}H_{20}O_4$ $[M+H]^+$: 253.1434, found: 253.1442; calculated for $C_{14}H_{20}O_4$ $[M+NH_4]^+$: 270.1700, found: 270.1706. FT-IR ($cm^{-1}$): 1717.5, 1583.5, 1454.9, 1402.4, 1277.1, 1166.9, 1087.8, 1012.1, 923.4.

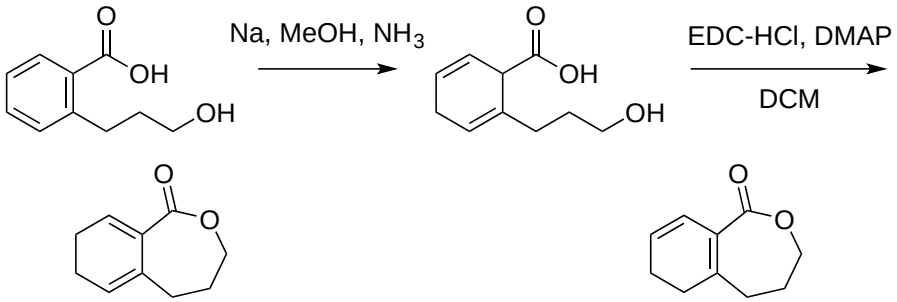



methyl (5a*R*,6*R*,8*R*)-1-oxo-1,4,5,6,7,8-hexahydro-3*H*-5a,8-ethanobenzo[*c*]oxepine-6-carboxylate
Chemical Formula: $C_{14}H_{18}O_4$
Molecular Weight: 250.29

Figure A.12 Diels Alder reaction to synthesize 7-membered ring lactone core.

Tricyclic lactones were synthesized by a Diels Alder reaction with the 4,5,6,7-alkene lactone isomer. Diene lactone (100 mg, 0.6 mmol), methyl acrylate (20 equiv., 12.2 mmol, 1g, 1.1 mL) and hydroquinone (20 mol%, 0.12 mmol, 13 mg) were combined in a pressure tube with ample headspace. This mixture was sparged with $N_2$ while stirring, and then heated at 140°C for 2 days. Excess methyl acrylate was evaporated, and then the mixture was purified by column chromatography (TLC: Rf = 0.25 in 1:1 Ethyl Acetate: Hexanes) Stain: $KMnO_4$ (bright yellow). The two regioisomers co-elute during this purification. However, the desired product is insoluble in diethyl ether. To the product mixture (after one column) was added diethyl ether, and the product was collected via filtration. The lower spot is the major product, the more congested product. Yield: 60%, 2:1 d.r. The desired product was confirmed by X-ray diffraction as **fda** (Appendix crystal – e).

$^1$H NMR (401 MHz, $CDCl_3$) δ 7.14 (d, *J* = 6.9 Hz, 1H), 4.21 (dd, *J* = 12.7, 6.6 Hz, 1H), 4.13 – 4.02 (m, 1H), 3.57 (s, 3H), 2.84 – 2.75 (m, 1H), 2.50 (dd, *J* = 10.2, 5.4 Hz, 1H), 2.15 – 1.90 (m, 3H), 1.80 – 1.66 (m, 2H), 1.63 – 1.33 (m, 4H), 1.27 (tdd, *J* = 15.1, 10.5, 5.0 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 174.10, 170.70, 144.10, 139.14, 65.13, 51.58, 49.74, 38.41, 31.33, 30.12, 28.75, 27.28, 24.79, 23.05. HRMS (ESI+): calculated for $C_{14}H_{18}O_4$ $[M+H]^+$: 251.1278, found: 251.1282; calculated for $C_{14}H_{18}O_4$ $[M+NH_4]^+$: 268.1543, found: 268.1544. IR ($cm^{-1}$): 1726.1, 1705.2, 1432.8, 1290.2, 1247.3, 1220.4, 1185.1, 1156.6, 1119.1, 1068.2, 1060.4, 1029.7, 1013.8, 987.9, 966.6, 924.3, 856.8, 756.0, 686.0.



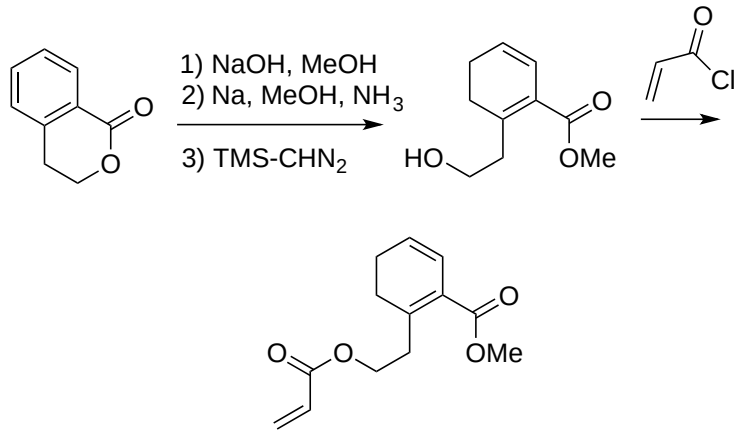

4,5,7,8-tetrahydrobenzo[*c*]oxepin-1(3*H*)-one
Chemical Formula: $C_{10}H_{12}O_2$
Molecular Weight: 164.20

4,5,6,7-tetrahydrobenzo[*c*]oxepin-1(3*H*)-one
Chemical Formula: $C_{10}H_{12}O_2$
Molecular Weight: 164.20

Figure A.13 Birch reduction and EDC coupling to form the 7-membered ring DA precursor.

To 25 mL of $NH_3$ (liquid, condensed with a dry ice/acetone cold finger and jacketed addition funnel), while stirring, was added a solution of the aromatic carboxy-alcohol (1.26 g, 7 mmol) in MeOH (1.75 M, 4 mL), followed by slow addition of sodium metal segments (3 equiv., 20.9 mmol, 480 mg). The solution turned blue and remained blue for 1 hour, followed by careful dropwise addition of MeOH (2 mL) and $H_2O$ (15 mL). Stirred at room temperature for 12 hours, the solution was brought to pH 2 with 1 M HCl and then extracted with Ethyl Acetate, washed with brine, dried with $Na_2SO_4$. The crude reaction mixture was dissolved in dry DCM (10 mL) and added EDC-HCl (1.2 equiv., 8.2 mmol, 1.57 g), followed by DMAP (5 mol%, 0.37 mmol, 45 mg), and stirred for 1 hour at room temperature. The reaction was washed with water (2x), dried with $Na_2SO_4$, and purified by column chromatography (Ethyl Acetate: Hexanes, 2:8). A mixture of alkene isomers was made. The 4,5,7,8-isomer was made in 41% yield.

$^1$H NMR (500 MHz, $CDCl_3$) δ 6.71 (t, *J* = 4.5 Hz, 1H), 5.60 (t, *J* = 4.1 Hz, 1H), 4.21 (t, *J* = 6.1 Hz, 4H), 2.36 – 2.31 (m, 2H), 2.24 – 2.16 (m, 2H), 1.93 – 1.84 (m, 2H). The 4,5,6,7 isomer was obtained in 17% yield. $^1$H NMR (500 MHz, $CDCl_3$) δ 6.22 (d, *J* = 9.7 Hz, 1H), 5.91 – 5.76 (m, 1H), 4.24 (t, *J* = 6.0 Hz, 2H), 2.42 (t, *J* = 7.4 Hz, 2H), 2.34 (dd, *J* = 19.2, 9.6 Hz, 2H), 2.23 (ddd, *J* = 10.3, 7.5, 3.2 Hz, 2H), 2.11 – 2.02 (m, 2H).

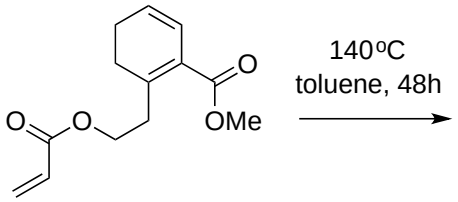


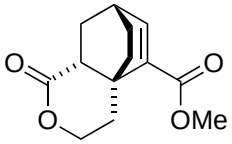

methyl 2-(2-(acryloyloxy)ethyl)cyclohexa-
1,5-diene-1-carboxylate
Chemical Formula: $C_{13}H_{16}O_4$
Molecular Weight: 236.27

Figure A.14 Preparation of Intramolecular Diels Alder substrate.

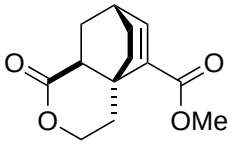
Isochromanone (5g, 34 mmol) was dissolved in MeOH (30 mL) and 2 M NaOH (30 mL) and refluxed with a chilled condenser for 2 hours. Excess MeOH was removed by rotary evaporation, and then submerging the round bottom flask in liquid nitrogen froze the aqueous solution prior to water removal by the lyophilizer. The white/cream solid was transferred to a 3-neck round bottom flask for the Birch reduction. To 25 mL of $NH_3$ (liquid, condensed with a dry ice/acetone cold finger and jacketed addition funnel), while stirring, was added a solution of the aromatic carboxy-alcohol (1.26 g, 7 mmol) in MeOH (1.75 M, 4 mL), followed by slow addition of sodium metal segments (3 equiv., 20.9 mmol, 480 mg). The solution turned blue and remained blue for 1 hour, followed by careful dropwise addition of MeOH (2 mL) and $H_2O$ (15 mL). Stirred at room temperature for 12 hours, the solution was brought to pH 2 with 1 M HCl and then extracted with Ethyl Acetate, washed with brine, dried with $Na_2SO_4$. The crude reaction was dissolved in 10 mL of DCM under $N_2$, chilled in a water ice bath, and then added 2M TMS-diazomethane in $Et_2O$ solution dropwise until a yellow color persisted. The mixture was evaporated and then purified by Biotage chromatography (EtOAc: Hexanes, 3:7). The alcohol was dissolved in DCM (30 mL) with triethylamine (1.5 equiv., 50 mmol, 7 mL) and acrolyl chloride (1.5 equiv., 50 mmol, 4 mL) was added dropwise with an ice water cooling bath. The mixture was stirred at room temperature for 12 hours, and then washed with sat. $NaHCO_3$ solution and water, dried with $MgSO_4$, evaporated, and then purified by column chromatography (EtOAc: Hexanes, 2:8).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.38 (dd, $J$ = 17.3, 1.5 Hz, 1H), 6.32 (dt, $J$ = 9.8, 1.9 Hz, 1H), 6.10 (dd, $J$ = 17.3, 10.4 Hz, 1H), 5.88 – 5.77 (m, 2H), 4.34 (t, $J$ = 6.9 Hz, 2H), 3.74 (s, 3H), 2.92 (t, $J$ = 6.9 Hz, 2H), 2.32 (t, $J$ = 9.4 Hz, 2H), 2.16 – 2.08 (m, 2H).




methyl (4a*R*,7*R*,8a*R*)-1-oxo-1,3,4,7,8,8a-hexahydro-4a,7-ethanoisochromene-5-carboxylate
Chemical Formula: $C_{13}H_{16}O_4$
Molecular Weight: 236.27

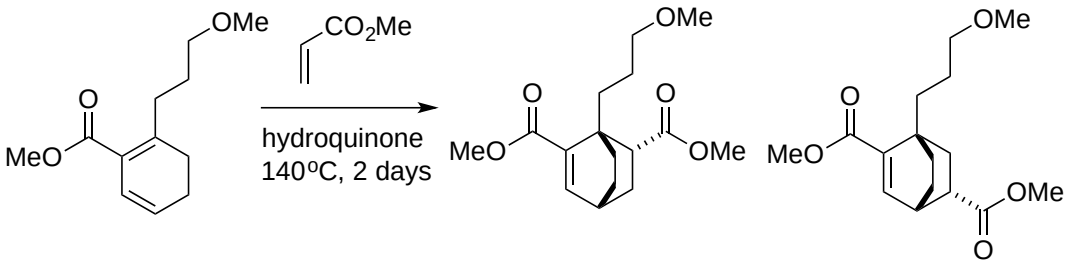



methyl (4a*R*,7*R*,8a*S*)-1-oxo-1,3,4,7,8,8a-hexahydro-4a,7-ethanoisochromene-5-carboxylate
Chemical Formula: $C_{13}H_{16}O_4$
Molecular Weight: 236.27

Figure A.15 Intramolecular Diels Alder.

The IMDA substrate (50 mg, 0.21 mmol) and hydroquinone (20 mol%, 0.04 mmol, 5 mg) were dissolved in toluene (2 mL) in a pressure tube, and then sparged with $N_2$ for 15 minutes. The tube was securely sealed, a safety shield was placed in front of the reaction, and then it was heated to 140°C for 48 hours. The mixture was evaporated and then purified by Biotage flash chromatography ($SiO_2$, Ethyl Acetate: Hexanes, 4:6). The cis-lactone:

$^1$H NMR (401 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.0 Hz, 1H), 4.43 (dd, *J* = 7.8, 5.0 Hz, 2H), 3.71 (s, 3H), 3.16 (dt, *J* = 14.2, 5.0 Hz, 1H), 2.83 (tt, *J* = 5.6, 2.8 Hz, 1H), 2.43 (dd, *J* = 9.6, 6.2 Hz, 1H), 2.02 – 1.92 (m, 2H), 1.84 (dd, *J* = 14.5, 7.5 Hz, 1H), 1.75 – 1.64 (m, 1H), 1.62 – 1.52 (m, 2H), 1.46 (td, *J* = 11.9, 4.5 Hz, 1H), 1.35 (ddd, *J* = 14.7, 8.9, 3.1 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.58, 165.33, 149.44, 134.13, 67.09, 51.53, 44.63, 37.91, 34.69, 30.84, 29.90, 28.14, 24.58. The trans-lactone: $^1$H NMR (401 MHz, $CDCl_3$) δ 7.35 (d, *J* = 6.9 Hz, 1H), 4.41 (t, *J* = 6.2 Hz, 2H), 3.74 (s, 3H), 3.03 (dt, *J* = 14.9, 5.7 Hz, 1H), 2.78 (d, *J* = 4.5 Hz, 1H), 2.40 (ddd, *J* = 11.4, 6.0, 2.1 Hz, 1H), 2.21 (ddd, *J* = 13.3, 6.0, 1.6 Hz, 1H), 2.05 (dt, *J* = 14.8, 6.6 Hz, 1H), 1.72 (m, 3H), 1.32 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 174.12, 165.38, 147.59, 138.41, 66.31, 51.51, 44.86, 37.22, 30.45, 30.03, 29.63, 26.34, 25.68.

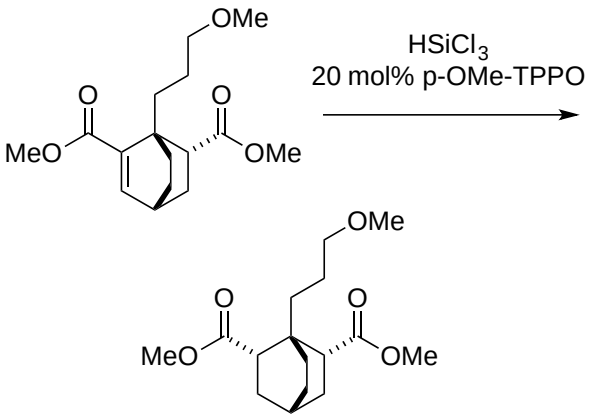



dimethyl (1*R*,4*R*,6*R*)-1-(3-methoxypropyl)bicyclo[2.2.2]oct-2-ene-2,6-dicarboxylate
Chemical Formula: $C_{16}H_{24}O_5$
Molecular Weight: 296.36

Figure A.16 Open chain system Diels Alder.

Diene ester/ether (100 mg, 0.48 mmol, 1 equiv.), methyl acrylate (1 mL, 9.5 mmol, 20 equiv.), and hydroquinone (11 mg, 0.1 mmol, 0.2 equiv.) were combined in a pressure tube with ample headspace. This mixture was heated at 140 °C for 2 days. Excess methyl acrylate was removed under pressure, and then the remaining oil was purified by column chromatography. Yield: 60%, 2:1 d.r.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.0 Hz, 1H), 3.67 (s, 3H), 3.57 (s, 3H), 3.43 – 3.30 (m, 2H), 3.29 (s, 3H), 2.71 (m, 1H), 2.58 (dd, *J* = 9.8, 5.5 Hz, 1H), 2.13 (td, *J* = 12.7, 3.5 Hz, 1H), 1.88 (ddd, *J* = 12.5, 9.9, 2.6 Hz, 1H), 1.46 (m, 8H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.07, 165.83, 145.60, 136.44, 73.53, 58.51, 51.39, 51.26, 47.25, 41.06, 31.99, 30.54, 30.37, 30.01, 25.24, 24.07. HRMS (ESI+): calculated for $C_{16}H_{24}O_5$ $[M+H]^+$: 297.1697, found: 297.1703. IR ($cm^{-1}$): 2947.9, 2867.7, 1716.0, 1433.4, 1240.7, 1190.5, 1161.5, 1119.1, 1081.7, 955.6, 750.7.

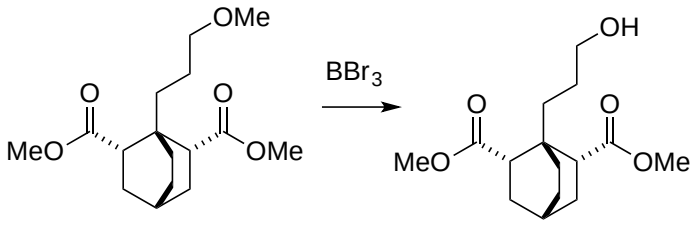



dimethyl (1*s*,2*R*,4*s*,6*S*)-1-(3-methoxypropyl)bicyclo[2.2.2]octane-2,6-dicarboxylate
Chemical Formula: $C_{16}H_{26}O_5$
Molecular Weight: 298.38

Figure A.17 Reduction of open chain bicyclic core.

Under nitrogen, a 5 mL flask equipped with a magnetic stir bar was added Michael acceptor (50 mg, 0.17 mmol, 1 equiv.), O=P(4-OMe-Ph)$_3$ (12 mg, 0.03 mmol, 0.2 equiv.), and 1 mL DCM. To this solution $HSiCl_3$ (40 µL, 0.4 mmol, 2.5 equiv.) was added dropwise. The reaction vial was removed from nitrogen, sealed with tape and parafilm, and heated to 30 °C in an aluminum heating block for 48 hours. After cooling to room temperature, the reaction was diluted with 2 mL of ethyl acetate and quenched with a few drops of saturated sodium bicarbonate solution. The crude reaction mixture was dried over sodium sulfate, filtered, and concentrated, which was purified by flash chromatography (EtOAc/hexanes).

$^1$H NMR (400 MHz, $CDCl_3$) δ 3.65 (d, *J* = 14.3 Hz, 6H), 3.40 – 3.26 (m, 5H), 2.45 (dd, *J* = 10.3, 6.5 Hz, 2H), 2.09 (dd, *J* = 12.6, 5.7 Hz, 2H), 1.84 – 1.37 (m, 11H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.09, 73.57, 58.48, 51.30, 43.51, 36.45, 33.19, 32.70, 29.05, 25.00, 23.85, 23.61. HRMS (ESI+): calculated for $C_{16}H_{25}O_5$ $[M+H]^+$: 299.1853, found: 299.1860. FT-IR ($cm^{-1}$): 2948.1, 1727.7, 1433.8, 1196.2, 1170.9, 1117.7, 1082.8.

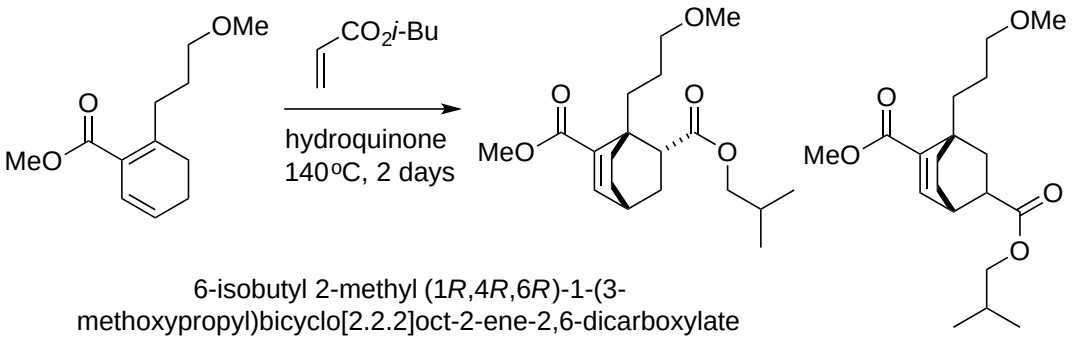



dimethyl (1*s*,2*R*,4*s*,6*S*)-1-(3-hydroxypropyl)bicyclo[2.2.2]octane-2,6-dicarboxylate
Chemical Formula: $C_{15}H_{24}O_5$
Molecular Weight: 284.35

Figure A.18 Conversion of methyl ether to alcohol by boron tribromide.

To a solution of the symmetrical ether diester (10 mg, 0.03 mmol) in DCM (2 mL), cooled to -78 °C, was added $BBr_3$ solution dropwise (2 equiv., 0.06 mmol, 1.0 M in Hexanes, 70 µL). The reaction flask was transferred to a 0°C ice bath, and stirred for 30 minutes. Saturated sodium bicarbonate solution was added dropwise (2 mL), and then stirred for 10 minutes at ambient temperature. The mixture was extracted with DCM (2x), washed with water, and then dried with $Na_2SO_4$.

$^1$H NMR (400 MHz, $CDCl_3$) δ 3.75 – 3.58 (m, 8H), 2.47 (dd, *J* = 10.5, 6.4 Hz, 2H), 2.10 (dd, *J* = 12.8, 5.8 Hz, 2H), 1.85 – 1.51 (m, 10H), 1.48 – 1.38 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 175.10, 63.50, 51.38, 43.57, 36.45, 33.18, 32.42, 29.06, 26.95, 24.98, 23.61. HRMS (ESI+): calculated for $C_{15}H_{24}O_5$ $[M+H]^+$: 285.1697, found: 285.1702. FT-IR ($cm^{-1}$): 3408.6, 2948.5, 1724.7, 1434.5, 1197.9, 1172.1, 1022.4.

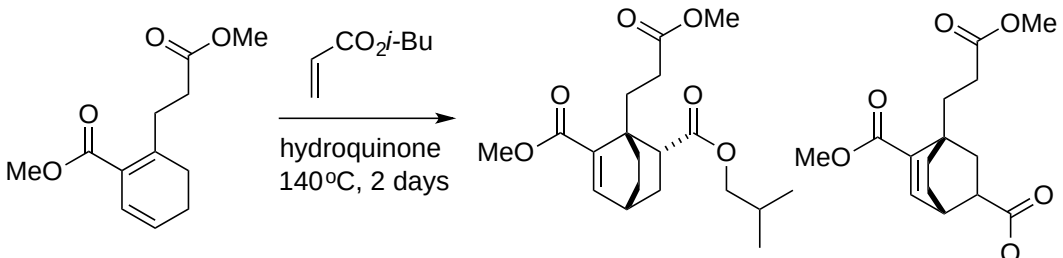



6-isobutyl 2-methyl (1*R*,4*R*,6*R*)-1-(3-methoxypropyl)bicyclo[2.2.2]oct-2-ene-2,6-dicarboxylate
Chemical Formula: $C_{19}H_{30}O_5$
Molecular Weight: 338.44

Figure A.19 Open chain system Diels Alder with isobutyl acrylate.

Diene ester/ether (100 mg, 0.48 mmol, 1 equiv.), isobutyl acrylate (1.4 mL, 9.5 mmol, 20 equiv.), and hydroquinone (11 mg, 0.1 mmol, 0.2 equiv.) were combined in a pressure tube with ample headspace. This mixture was heated at 140 °C for 2 days. Excess isobutyl acrylate was removed under pressure, and then the remaining oil was purified by Biotage column chromatography ($SiO_2$, 20% to 50% EtOAc in Hexanes). Yield: 60%, 2:1 d.r.

$^1$H NMR (700 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.0 Hz, 1H), 3.82 (dd, *J* = 10.6, 6.7 Hz, 1H), 3.73 (dd, *J* = 10.6, 6.5 Hz, 1H), 3.69 (s, 3H), 3.41 (dd, *J* = 14.3, 7.8 Hz, 1H), 3.37 – 3.34 (m, 1H), 3.32 (s, 3H), 2.75 – 2.72 (m, 1H), 2.60 (dd, *J*= 9.8, 5.5 Hz, 1H), 2.24 – 2.17 (m, 1H), 1.95 – 1.90 (m, 1H), 1.86 (m, 1H), 1.72 – 1.28 (m, 8H), 0.89 (d, *J* = 6.8 Hz, 6H). $^{13}$C NMR (176 MHz, $CDCl_3$) δ 174.71, 165.78, 145.84, 136.36, 73.55, 70.56, 58.54, 51.25, 47.68, 41.05, 32.06, 30.63, 30.55, 30.08, 27.59, 25.35, 24.10, 19.11, 19.10. HMRS (ESI+): calculated for $C_{19}H_{30}O_5$ $[M+H]^+$: 339.2166, found: 339.2173; calculated for $C_{19}H_{30}O_5$ $[M+NH_4]^+$: 356.2431, found: 356.2436. FT-IR ($cm^{-1}$): 2949.9, 1716.9, 1434.0, 1241.1, 1158.0, 1120.4, 1081.7, 750.1.

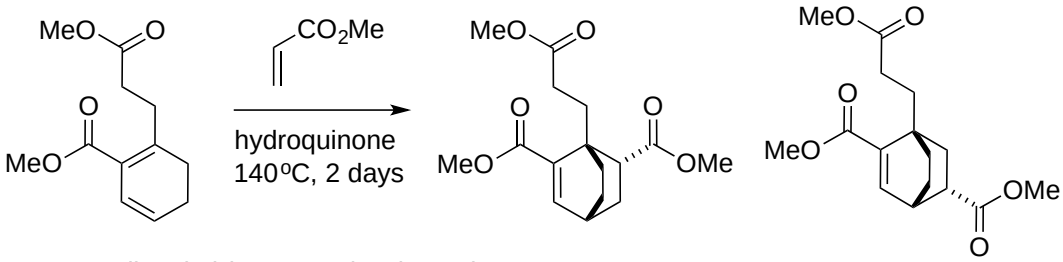



6-isobutyl 2-methyl (1*R*,4*R*,6*R*)-1-(3-methoxy-3-oxopropyl)bicyclo[2.2.2]oct-2-ene-2,6-dicarboxylate
Chemical Formula: $C_{19}H_{28}O_6$
Molecular Weight: 352.43

Figure A.20 Open chain di-ester system Diels Alder with isobutyl acrylate.

The general Diels Alder procedure was used. Yield: 60%, 2:1 d.r.

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.1 Hz, 1H), 3.82 (dd, *J* = 10.6, 6.7 Hz, 1H), 3.74 (dd, *J* = 10.6, 6.6 Hz, 1H), 3.69 (s, 3H), 3.65 (s, 3H), 2.75 (dd, *J* = 6.4, 3.1 Hz, 1H), 2.66 – 2.54 (m, 2H), 2.39 (t, *J* = 8.0 Hz, 2H), 2.06 – 1.80 (m, 3H), 1.63 – 1.54 (m, 1H), 1.52 – 1.45 (m, 1H), 1.44 – 1.32 (m, 2H), 1.30 – 1.20 (m, 1H), 0.88 (d, *J* = 6.7 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 174.41, 174.29, 165.52, 146.36, 135.69, 70.69, 51.53, 51.31, 47.81, 40.82, 31.95, 30.37, 30.36, 30.08, 29.36, 27.55, 23.97, 19.07. HMRS (ESI+): calculated for $C_{19}H_{28}O_6$ $[M+H]^+$: 353.1959, found: 353.1957; calculated for $C_{19}H_{28}O_6$ $[M+NH_4]^+$: 370.2224, found: 370.2220; calculated for $C_{19}H_{28}O_6$ $[M+Na]^+$: 375.1778, found: 375.1777. FT-IR ($cm^{-1}$): 1715.1, 1434.7, 1242.3, 1160.5, 1082.7, 1063.0, 1019.8, 750.1.

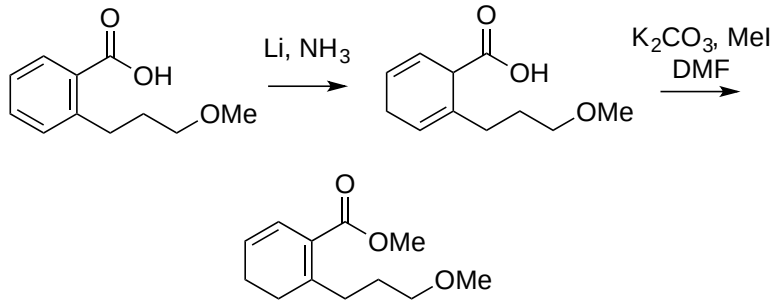



dimethyl (1*R*,4*R*,6*R*)-1-(3-methoxy-3-oxopropyl)bicyclo[2.2.2]oct-2-ene-2,6-dicarboxylate
Chemical Formula: $C_{16}H_{22}O_6$
Molecular Weight: 310.35

Figure A.21 Open chain di-ester system Diels Alder with methyl acrylate.

The general Diels Alder procedure was used. Yield: 60%, 2:1 d.r.

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.0 Hz, 1H), 3.69 (s, 3H), 3.64 (s, 3H), 3.61 (s, 3H), 2.75 (s, 1H), 2.55 (ddd, *J* = 20.1, 13.2, 7.9 Hz, 2H), 2.43 – 2.32 (m, 2H), 1.95 (ddd, *J* = 29.4, 18.8, 9.4 Hz, 2H), 1.64 – 1.53 (m, 1H), 1.51 – 1.31 (m, 3H), 1.29 – 1.19 (m, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 174.81, 174.33, 165.57, 146.23, 135.73, 51.57, 51.50, 51.36, 47.47, 40.87, 31.89, 30.29, 30.27, 30.03, 29.28, 23.94. HMRS (ESI+): calculated for $C_{16}H_{22}O_6$ $[M+H]^+$: 311.1489, found: 311.1497; calculated for $C_{16}H_{22}O_6$ $[M+NH_4]^+$: 328.1755, found: 328.1759. FT-IR ($cm^{-1}$): 1713.5, 1433.7, 1242.0, 1191.6, 1162.2, 1081.5, 750.6.

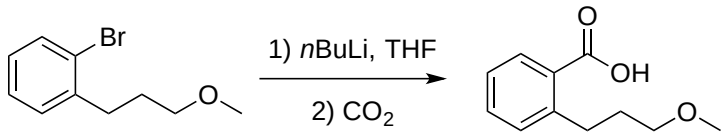



methyl 2-(3-methoxypropyl)cyclohexa-1,5-diene-1-carboxylate
Chemical Formula: $C_{12}H_{18}O_3$
Exact Mass: 210.13

Figure A.22 Synthesis of open-chain Diels Alder substrate by Birch reduction and methylation.

To 25 mL of $NH_3$ (liquid, condensed with a dry ice/acetone cold finger and jacketed addition funnel), while stirring, was added a solution of the aromatic carboxy-ether (1.36 g, 7 mmol) in MeOH (1.75 M, 4 mL), followed by slow addition of sodium metal segments (3 equiv., 20.9 mmol, 480 mg). The solution turned blue and remained blue for 1 hour, followed by careful dropwise addition of MeOH (2 mL) and $H_2O$ (15 mL). Stirred at room temperature for 12 hours, the solution was brought to pH 2 with 1 M HCl and then extracted with Ethyl Acetate, washed with brine, dried with $Na_2SO_4$. The crude reaction mixture was dissolved in DMF (15 mL), and then added $K_2CO_3$ (1 equiv., 7 mmol, 1g) and MeI dropwise (2.5 equiv., 17.5 mmol, 2.5g, 1 mL). The reaction was stirred for 6 hours, added 15 mL of brine, and extracted with EtOAc (3x). The combined organic fractions were washed with brine, water, and dried with $Na_2SO_4$. The crude mixture was purified by Biotage flash chromatography (100g $SiO_2$, 20% EtOAc in Hexanes).

HMRS (ESI+): calculated for $C_{12}H_{18}O_3$ $[M+H]^+$: 211.1329, found: 211.1329. FT-IR ($cm^{-1}$): 1715.1, 1433.5, 1254.0, 1235.8, 1196.5, 1114.3, 1079.5, 701.7.

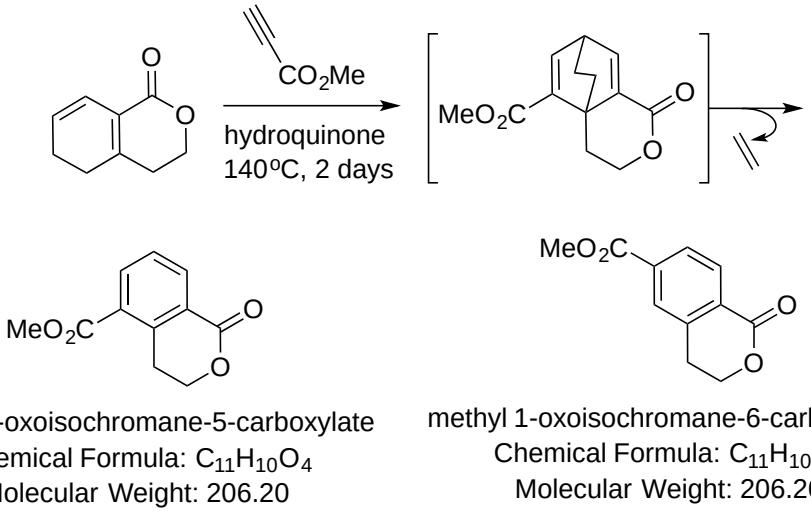



2-(3-methoxypropyl)benzoic acid
Chemical Formula: $C_{11}H_{14}O_3$
Molecular Weight: 194.23

Figure A.23 Synthesis of open-chain Birch reduction substrate.

To a solution of the aryl bromide (4.85g, 21.2 mmol) stirred in 170 mL THF at -78°C was added n-Butyl Lithium solution (1.12 equiv., 2.5M in Hexanes, 23.75 mmol, 9.5 mL) dropwise and then stirred for an additional 15 minutes at -78°C. Gaseous $CO_2$ was bubbled into the reaction mixture for 20 minutes by evaporating dry ice in a flask adapted with an outlet connected to a tube and needle. 1M HCl was added, the mixture was extracted with Ethyl Acetate, washed with brine, water, dried with $MgSO_4$, and purified by Biotage flash chromatography (EtOAc: Hexanes).

HMRS (ESI+): calculated for $C_{11}H_{14}O_3$ $[M+H]^+$: 217.0835, found: 217.0840. FT-IR ($cm^{-1}$): 2926.5, 2869.1, 1687.7, 1451.8, 1236.6, 1104.9, 883.4, 745.8, 705.2, 647.0.



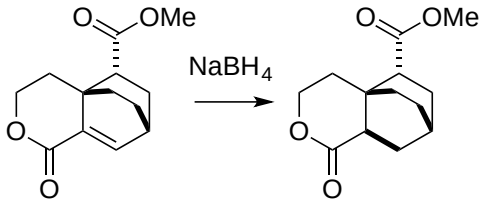

methyl 1-oxoisochromane-5-carboxylate
Chemical Formula: $C_{11}H_{10}O_4$
Molecular Weight: 206.20

methyl 1-oxoisochromane-6-carboxylate
Chemical Formula: $C_{11}H_{10}O_4$
Molecular Weight: 206.20

Figure A.24 Diels Alder with an alkyne dienophile.

Diene lactone (100 mg, 0.67 mmol, 1 equiv.), methyl propiolate (1.2 mL, 13.3 mmol, 20 equiv.), and hydroquinone (15 mg, 0.13 mmol, 0.2 equiv.) were combined in a pressure tube with ample headspace. This mixture was heated at 140 °C for 2 days. Excess methyl propiolate was removed under pressure, and then the remaining oil was purified by column chromatography to yield a 2:1 mixture of isomers. The 5-isomer was made in 40% yield.

$^1$H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 7.8 Hz, 1H), 8.21 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 4.51 (t, *J* = 6.1 Hz, 2H), 3.93 (s, 3H), 3.52 (t, *J* = 6.1 Hz, 2H). The 6-isomer was obtained in 20% yield. $^1$H NMR (700 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.1 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.93 (s, 1H), 4.55 (t, *J* = 6.0 Hz, 2H), 3.93 (s, 3H), 3.11 (t, *J* = 6.0 Hz, 2H). $^{13}$C NMR (176 MHz, $CDCl_3$) δ 165.85, 164.18, 139.54, 134.37, 130.45, 128.75, 128.43, 128.42, 67.26, 52.55, 27.65. HRMS (ESI+): calculated for $C_{11}H_{10}O_4$ $[M+H]^+$: 207.0652, found: 207.0655. FT-IR ($cm^{-1}$): 1708.0, 1296.3, 1267.1, 1242.9, 1215.3, 1185.7, 1115.1, 1082.5, 954.3, 746.5, 693.5, 638.4.




methyl (4a*R*,5*R*,7*R*,8a*R*)-1-oxooctahydro-4a,7-ethanoisochromene-5-carboxylate
Chemical Formula: $C_{13}H_{18}O_4$
Molecular Weight: 238.28

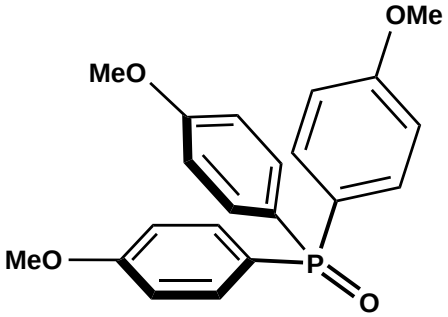
Figure A.25 Sodium borohydride reduction of Diels Alder product.

The Alkene-Lactone-Ester (177 mg, 0.75 mmol) was dissolved in 10 mL of THF and 2 mL of $H_2O$. Solid $NaBH_4$ (10 equiv., 7.5 mmol) was added slowly, then stirred under $N_2$ for 4 hours at ambient temperature. The reaction was brought to 0 °C, then saturated $NH_4Cl$ solution was added slowly until completely quenched. The mixture was extracted with EtOAc (3x), and then washed with brine, water, and dried with $Na_2SO_4$.

$^1$H NMR (700 MHz, $CDCl_3$) δ 4.22 (ddd, *J* = 11.7, 5.6, 2.7 Hz, 1H), 4.16 (td, *J* = 11.9, 3.3 Hz, 1H), 3.65 (s, 3H), 2.51 (dd, *J* = 9.9, 5.5 Hz, 1H), 2.39 (t, *J* = 9.6 Hz, 1H), 2.08 (t, *J* = 11.5 Hz, 1H), 2.01 (ddd, *J* = 14.6, 12.1, 5.6 Hz, 1H), 1.90 – 1.81 (m, 4H), 1.71 – 1.64 (m, 3H), 1.59 – 1.50 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.05, 174.40, 63.86, 51.28, 46.14, 39.81, 36.05, 32.20, 32.08, 30.03, 26.80, 24.89, 23.76. HRMS (ESI+): calculated for $C_{13}H_{18}O_4$ $[M+H]^+$: 239.1278, found: 239.1286; calculated for $C_{13}H_{18}O_4$ $[M+NH_4]^+$: 256.1549, found: 256.1549. FT-IR ($cm^{-1}$): 2930.4, 2870.0, 1747.3, 1729.3, 1426.0, 1238.7, 1177.4, 1162.8, 1076.9, 1008.7, 933.6, 851.6.

## APPENDIX B: Chapter IV Supporting Information

Table B.1 4-OMe-TPPO catalyst



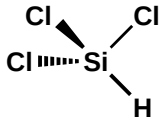

Total Free Energy: -1455.16404091342

47

| | | | |
|---|---|---|---|
| P | -0.52974438 | -0.14990997 | -0.00685070 |
| O | 0.27455160 | -0.94470199 | 0.99250026 |
| C | -2.33831139 | -0.18958236 | 0.25998977 |
| C | -0.03870850 | 1.61229735 | 0.00516440 |
| C | 0.90154281 | -1.48872218 | -1.97155964 |
| C | -1.15178059 | -0.51189938 | -2.77442303 |
| C | -0.87334601 | -0.96364517 | -4.06872131 |
| C | 1.19115682 | -1.94439615 | -3.25153278 |
| C | 0.30620027 | -1.68146658 | -4.30974916 |
| H | -1.58005836 | -0.75993332 | -4.86574673 |
| H | 2.09406595 | -2.51246482 | -3.45589040 |
| O | 0.67636374 | -2.17052649 | -5.52828424 |
| C | -3.03768427 | 0.87874390 | 0.84996672 |
| C | -3.04234320 | -1.37054779 | -0.01339561 |
| C | -4.40349444 | -1.49229276 | 0.27398999 |
| C | -4.39291584 | 0.77390279 | 1.14095099 |
| H | -2.51871794 | 1.80324357 | 1.08552093 |
| H | -2.52535307 | -2.21769727 | -0.45707476 |
| C | -5.08507980 | -0.41280981 | 0.85444995 |
| H | -4.91277532 | -2.42200157 | 0.04636721 |
| O | -6.41017930 | -0.41872027 | 1.17547116 |
| H | -4.93567036 | 1.59739729 | 1.59576548 |
| C | 0.89905361 | 2.01960207 | 0.97037458 |
| C | -0.51564839 | 2.56139571 | -0.90551734 |

| | | | |
|---|---|---|---|
| H | 1.28225695 | 1.28415845 | 1.67236483 |
| C | 1.33882313 | 3.33750239 | 1.02430401 |
| C | 0.85085103 | 4.28079487 | 0.10667898 |
| C | -0.08340676 | 3.88961615 | -0.86383005 |
| H | -0.47506306 | 4.59783300 | -1.58560576 |
| H | -1.23460238 | 2.27500781 | -1.66919985 |
| H | 2.06429666 | 3.65839135 | 1.76624076 |
| O | 1.34321495 | 5.54623818 | 0.23605698 |
| C | 0.90824880 | 6.54752327 | -0.67593368 |
| H | 1.42777396 | 7.46074831 | -0.38105179 |
| H | -0.17584718 | 6.70627221 | -0.60772471 |
| H | 1.17866381 | 6.29005367 | -1.70831508 |
| C | -7.16967255 | -1.59652911 | 0.92954685 |
| H | -8.18146299 | -1.37128293 | 1.27050952 |
| H | -6.77469357 | -2.45040172 | 1.49463947 |
| H | -7.19053920 | -1.84070394 | -0.14058836 |
| C | -0.16988304 | -1.93528714 | -6.64678076 |
| H | -1.15870287 | -2.38969981 | -6.50162613 |
| H | 0.32558920 | -2.40781148 | -7.49651652 |
| H | -0.28402053 | -0.86084813 | -6.84126914 |
| C | -0.27271557 | -0.75718205 | -1.71392087 |
| H | -2.08052198 | 0.02675046 | -2.60157310 |
| H | 1.57889956 | -1.70517863 | -1.14999135 |

Table B.2 Trichlorosilane ($HSiCl_3$)

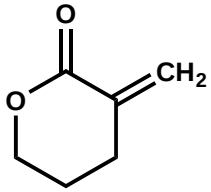



Total Free Energy: -1670.83173457694

5

| | | | |
|---|---|---|---|
| Si | 0.41558280 | 0.86061942 | -0.09378047 |
| Cl | 2.47034290 | 0.86579581 | -0.10301374 |
| Cl | -0.27384190 | -1.07162427 | 0.01572394 |
| H | -0.07344538 | 1.47859798 | -1.33418562 |
| Cl | -0.27324841 | 1.93627105 | 1.51525589 |

Table B.3 Substrate F: Alpha-methylene delta-valerolactone.

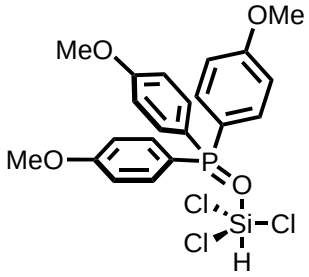



Substrate F: Total Free Energy: -383.903357241634

16

| | | | |
|---|---|---|---|
| C | -0.91492948 | -0.74545807 | 1.53403103 |
| C | -1.50082442 | -1.36996485 | 0.28404161 |
| C | 0.35706325 | 0.03586673 | 1.19333101 |
| C | -2.81337135 | -1.57204572 | 0.10584360 |
| O | 0.73816279 | -1.44578500 | -0.74223688 |
| H | 0.84375295 | 0.41242752 | 2.10150212 |
| H | 0.11792298 | 0.90255197 | 0.56303502 |
| C | 1.31544667 | -0.88628709 | 0.45877645 |
| H | 1.62550415 | -1.72048330 | 1.10257082 |
| H | 2.21279236 | -0.36600713 | 0.11511827 |
| C | -0.57938098 | -1.77031097 | -0.83964313 |
| O | -0.95793292 | -2.33355274 | -1.84468244 |
| H | -3.18659918 | -2.03085325 | -0.80404253 |
| H | -0.66049919 | -1.53656685 | 2.25625789 |
| H | -1.66112761 | -0.10632885 | 2.01952553 |
| H | -3.53588006 | -1.28281240 | 0.86561163 |

Table B.4 Trichlorosilane bound to 4-OMe-TPPO catalyst



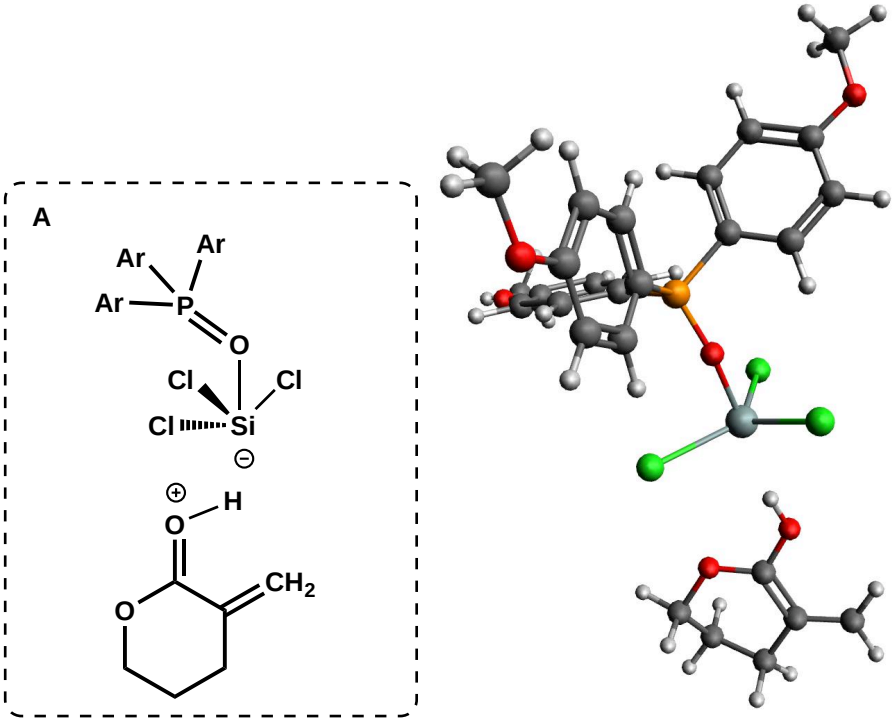

Free Energy: -3125.99824341344

52

| | | | |
|---|---|---|---|
| P | -0.53084416 | -0.23814006 | -0.06386658 |
| O | 0.34874599 | -1.06343794 | 0.90959596 |
| C | -2.30890994 | -0.33145624 | 0.24214452 |
| C | 0.00839092 | 1.48153064 | 0.10207026 |
| C | 1.03340051 | -1.38530466 | -2.04911921 |
| C | -1.14989756 | -0.63789642 | -2.77974908 |
| C | -0.85781806 | -1.03372279 | -4.08769383 |
| C | 1.33119016 | -1.78311333 | -3.34322574 |
| C | 0.38806547 | -1.61095922 | -4.37199761 |
| H | -1.60488941 | -0.89934946 | -4.86169768 |
| H | 2.28480370 | -2.24377317 | -3.58166215 |
| O | 0.77319267 | -2.04057847 | -5.60192680 |
| C | -3.01772140 | 0.75763117 | 0.78429040 |
| C | -2.99441426 | -1.53284732 | 0.00310708 |
| C | -4.35152805 | -1.65461259 | 0.29518275 |

| | | | |
|---|---|---|---|
| C | -4.37033768 | 0.64824143 | 1.07224767 |
| H | -2.50749662 | 1.69407024 | 0.98639618 |
| H | -2.46531473 | -2.39327008 | -0.39459962 |
| C | -5.04563311 | -0.56112387 | 0.83619900 |
| H | -4.84745654 | -2.59996988 | 0.10884095 |
| O | -6.36358178 | -0.57384805 | 1.16133683 |
| H | -4.92344877 | 1.48120518 | 1.49525924 |
| C | 0.59497755 | 1.91279586 | 1.30792134 |
| C | -0.15296810 | 2.39973682 | -0.94272666 |
| H | 0.74656231 | 1.20867335 | 2.11980857 |
| C | 0.99281518 | 3.23372565 | 1.46053654 |
| C | 0.82088947 | 4.15100730 | 0.40991634 |
| C | 0.24668401 | 3.72947340 | -0.79919136 |
| H | 0.11996626 | 4.41351570 | -1.63019310 |
| H | -0.58082169 | 2.08365977 | -1.89064737 |
| H | 1.44986460 | 3.57676591 | 2.38363731 |
| O | 1.24807741 | 5.41723988 | 0.65585229 |
| C | 1.13041910 | 6.39623731 | -0.37244571 |
| H | 1.53818613 | 7.31617118 | 0.04870517 |
| H | 0.08073365 | 6.55408115 | -0.65083209 |
| H | 1.71075538 | 6.11014277 | -1.25854237 |
| C | -7.10345831 | -1.78203037 | 0.99834531 |
| H | -8.11257215 | -1.55578712 | 1.34504397 |
| H | -6.67835459 | -2.59043433 | 1.60556016 |
| H | -7.13747831 | -2.08691648 | -0.05523006 |
| C | -0.13385387 | -1.91659063 | -6.69337143 |
| H | -1.04980594 | -2.49468757 | -6.51587328 |
| H | 0.39189440 | -2.32253463 | -7.55873703 |
| H | -0.38870203 | -0.86557892 | -6.87998353 |
| C | -0.21510660 | -0.80374565 | -1.75089422 |
| H | -2.12616186 | -0.20968968 | -2.56915908 |
| H | 1.75999804 | -1.54200991 | -1.25745414 |
| Si | 0.52508429 | -2.37785779 | 2.20312067 |
| Cl | -0.23067114 | -3.80953613 | 0.76744851 |
| H | 0.68206375 | -3.43056998 | 3.23102530 |
| Cl | -0.81611440 | -1.24072311 | 3.44694327 |
| Cl | 2.60647009 | -1.89371888 | 2.20398413 |

Table B.5 Transition State of Pathway A




Beginning E: -3509.894929
TS E: -3509.819569
Ending E: -3509.829200

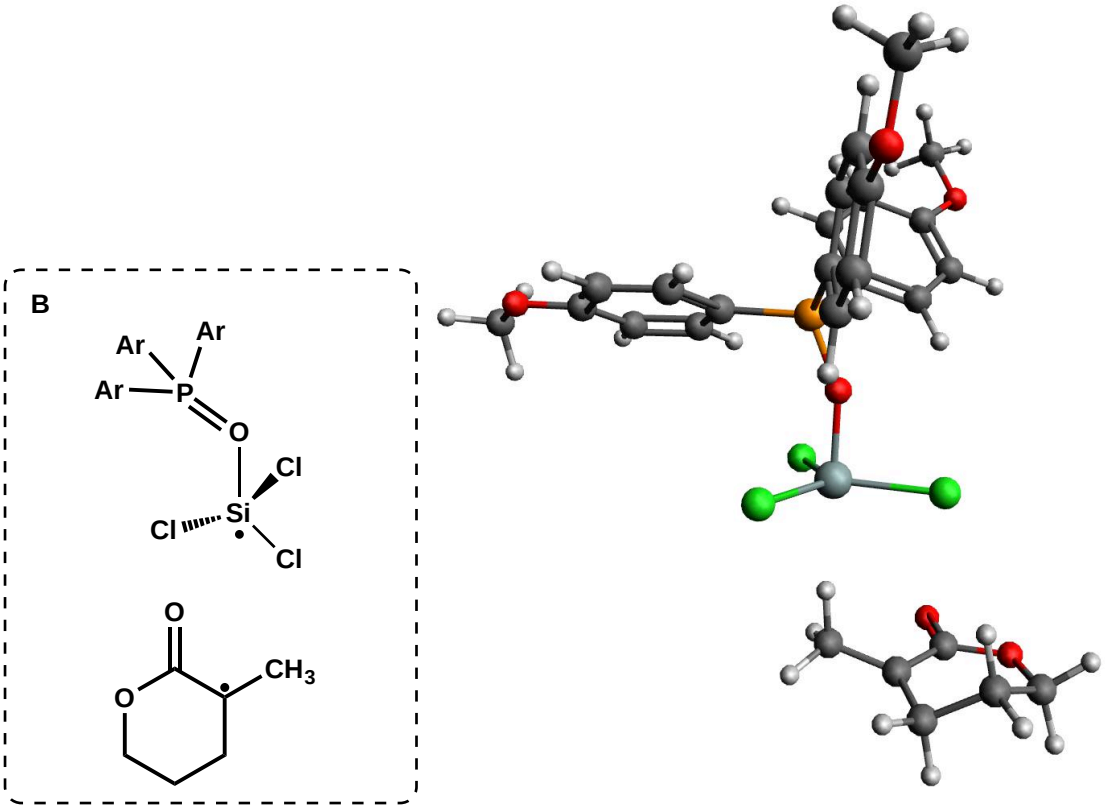
TS-A
68

C -3.292459 0.373421 0.096766
C -2.028239 -0.473521 0.072958
C -3.097697 1.665578 -0.700256
C -2.059160 -1.823124 0.267242
O -0.670655 1.508533 -0.376768
H -3.951589 2.341192 -0.571432
H -3.001871 1.453702 -1.773142
C -1.834952 2.356438 -0.206021
H -1.905238 2.611993 0.858763
H -1.588934 3.257712 -0.770367
C -0.781964 0.195580 -0.190582
O 0.281115 -0.513886 -0.402099
H -1.152099 -2.416783 0.275046
H -3.536063 0.635164 1.137164
H -4.132409 -0.220918 -0.279327
H -3.002657 -2.333783 0.438190
P 6.394339 1.530455 -0.987218
O 5.115902 0.853568 -0.445780

C 6.089440 2.915336 -2.104567
C 7.342661 2.153551 0.423372
C 7.200219 -1.075133 -1.439115
C 8.371007 0.582305 -2.762410
C 9.183983 -0.414881 -3.307526
C 7.998265 -2.071212 -1.980468
C 9.002418 -1.747543 -2.909180
H 9.941484 -0.144225 -4.034165
H 7.862361 -3.110153 -1.697016
O 9.743086 -2.793991 -3.364480
C 6.128021 4.236530 -1.615525
C 5.712002 2.697603 -3.438765
C 5.379713 3.767945 -4.270307
C 5.799158 5.305092 -2.434603
H 6.402608 4.427982 -0.583279
H 5.661125 1.689639 -3.840398
C 5.415467 5.077399 -3.766132
H 5.081983 3.568159 -5.293084
O 5.098250 6.187039 -4.482366
H 5.816261 6.324493 -2.061620
C 6.706444 2.497902 1.631576
C 8.724300 2.349336 0.299938
H 5.635401 2.349273 1.741198
C 7.445479 3.034931 2.679769
C 8.828602 3.241306 2.541919
C 9.471420 2.891304 1.345166
H 10.539261 3.026261 1.218366
H 9.240747 2.074114 -0.615369
H 6.968599 3.303196 3.617370
O 9.463553 3.781947 3.616618
C 10.862115 4.037839 3.527052
H 11.144175 4.475991 4.485205
H 11.084246 4.747809 2.720271
H 11.427779 3.110089 3.368121
C 4.631154 6.036403 -5.820096
H 4.411175 7.046785 -6.168698
H 3.718599 5.428490 -5.852725
H 5.400103 5.586951 -6.460770
C 10.795747 -2.544798 -4.289976
H 10.411471 -2.112372 -5.222490
H 11.241598 -3.518901 -4.496876
H 11.553929 -1.879573 -3.857755
C 7.385230 0.269639 -1.819196
H 8.516088 1.610036 -3.085868
H 6.422824 -1.336512 -0.726390
Si 3.380262 0.353476 -0.359267

Cl 4.022778 -1.325704 0.976530
Cl 3.429727 -0.108623 -2.601586
Cl 2.978881 2.449423 0.603035
H 1.259374 -0.130886 -0.291516

Table B.6 Transition State of Pathway B




Beginning E: -3509.899042
TS E: -3509.855765
Ending E: -3509.861563

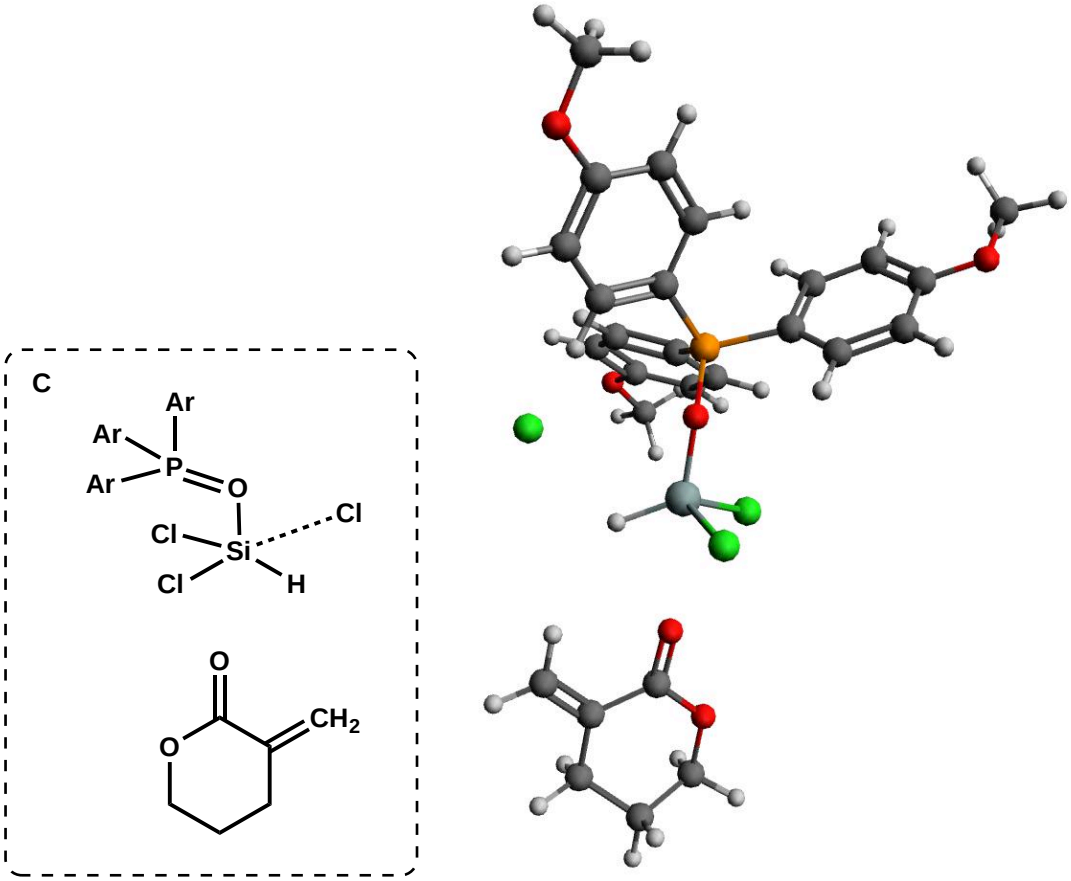
TS-B
68

C 0.218364 0.749215 -2.307580
C 0.457630 1.095178 -0.864429
C 0.945677 1.786596 -3.177683
C 0.916004 0.095917 0.110593
O 0.422855 3.471274 -1.422502
H 0.785361 1.606918 -4.248971
H 2.019720 1.713191 -2.973005
C 0.403749 3.166057 -2.831221
H -0.638680 3.254429 -3.169529
H 0.982933 3.964265 -3.305710
C 0.459941 2.495480 -0.455967

O 0.503620 2.862735 0.711209
H 0.641047 0.341283 1.139499
H -0.860798 0.801996 -2.535725
H 0.549566 -0.271693 -2.527864
H 0.614636 -0.925348 -0.146466
P 7.469134 0.289847 0.959658
O 6.081800 0.501539 0.281840
C 7.534346 -1.100190 2.102529
C 8.625184 -0.006894 -0.396232
C 7.364267 3.028401 1.365127
C 8.816615 1.824108 2.886726
C 9.192578 3.025185 3.491293
C 7.735637 4.224517 1.957795
C 8.653311 4.232424 3.023572
H 9.889196 3.004844 4.321323
H 7.319679 5.169218 1.621106
O 8.948726 5.453174 3.534916
C 8.150641 -2.313555 1.733488
C 6.914722 -1.010471 3.360392
C 6.908261 -2.095178 4.234336
C 8.150601 -3.397001 2.598848
H 8.632336 -2.410945 0.765775
H 6.408852 -0.097154 3.655445
C 7.526483 -3.297425 3.854567
H 6.410486 -1.997833 5.192039
O 7.576752 -4.410283 4.626869
H 8.620312 -4.335545 2.321821
C 8.161692 -0.586722 -1.593846
C 9.982947 0.312000 -0.275012
H 7.110736 -0.833786 -1.707802
C 9.042884 -0.841187 -2.635041
C 10.404455 -0.519353 -2.506265
C 10.876006 0.059293 -1.317877
H 11.920195 0.323823 -1.197645
H 10.361355 0.772367 0.633711
H 8.695588 -1.282166 -3.564298
O 11.180069 -0.798628 -3.584749
C 12.567027 -0.472333 -3.544279
H 12.967686 -0.777392 -4.511772
H 13.081163 -1.021855 -2.745673
H 12.715016 0.606175 -3.408927
C 6.929314 -4.401967 5.898826
H 7.087770 -5.398251 6.313366
H 5.854248 -4.214099 5.791928
H 7.375083 -3.652091 6.563833
C 9.857071 5.546354 4.629135

H 9.475277 5.009332 5.506294
H 9.931755 6.610188 4.857417
H 10.846949 5.159084 4.356747
C 7.906877 1.809776 1.821915
H 9.233471 0.895467 3.267040
H 6.640398 3.033265 0.555381
Si 4.327971 0.303446 0.180323
Cl 4.172898 1.972450 -1.218691
Cl 4.041394 0.761035 2.335681
Cl 4.533175 -1.746721 -0.671181
H 2.057849 0.070422 0.130250

Table B.7 Transition State of Pathway C




Beginning E: -3509.894774
TS E: -3509.877538
Ending E: -3509.883040

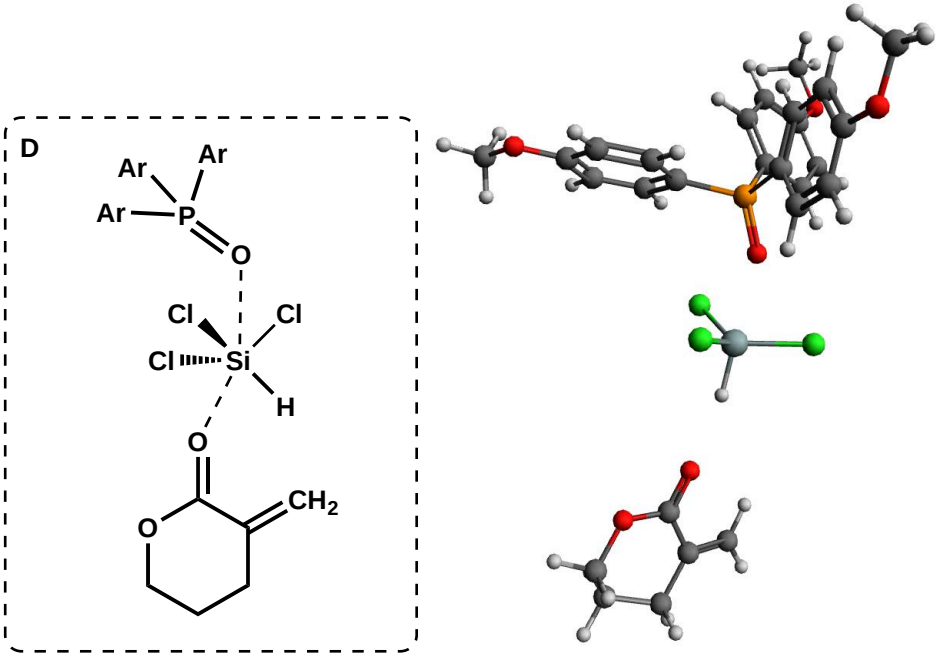
TS-C
68

C -2.225379 -1.608951 2.297850
C -0.806780 -1.470971 1.786462

C -3.037447 -0.350127 1.986190
C -0.066269 -2.511415 1.377947
O -0.959322 0.979464 2.000657
H -4.032373 -0.400931 2.445323
H -3.178150 -0.240542 0.902744
C -2.297572 0.858748 2.533405
H -2.219590 0.807084 3.628080
H -2.783482 1.800665 2.267295
C -0.190109 -0.101731 1.710326
O 0.954951 0.093020 1.359417
H 0.963984 -2.388366 1.060258
H -2.206643 -1.754759 3.389172
H -2.695292 -2.502520 1.870720
H -0.471186 -3.520851 1.381772
P 6.807954 0.599295 0.889509
O 5.412812 0.274394 0.181665
C 6.755785 0.391832 2.666983
C 8.003290 -0.456882 0.049267
C 6.742408 2.936854 -0.642426
C 8.228196 2.964842 1.268277
C 8.733419 4.203825 0.871001
C 7.230255 4.174684 -1.038504
C 8.244129 4.807319 -0.296134
H 9.502439 4.676937 1.470487
H 6.853251 4.665937 -1.930321
O 8.690706 5.991823 -0.787971
C 7.085802 -0.839908 3.272680
C 6.251489 1.433156 3.466196
C 6.042737 1.252498 4.828790
C 6.893839 -1.018361 4.633896
H 7.437390 -1.673390 2.676931
H 5.988061 2.387599 3.024493
C 6.343812 0.011209 5.413732
H 5.626031 2.065681 5.410959
O 6.123070 -0.282004 6.720151
H 7.104930 -1.974997 5.099956
C 7.664161 -1.779911 -0.308003
C 9.269271 0.044087 -0.289087
H 6.697334 -2.196963 -0.021099
C 8.587093 -2.573310 -0.974587
C 9.852673 -2.065857 -1.312910
C 10.195692 -0.750372 -0.963541
H 11.162304 -0.332316 -1.218578
H 9.545736 1.065979 -0.049985
H 8.340937 -3.594964 -1.247324
O 10.676491 -2.915564 -1.982470

C 11.961566 -2.454371 -2.387506
H 12.423315 -3.292204 -2.911690
H 12.577789 -2.180535 -1.521441
H 11.878681 -1.596968 -3.067751
C 5.414234 0.657434 7.524353
H 5.291994 0.178780 8.497004
H 4.428469 0.875825 7.094511
H 5.980965 1.589317 7.643985
C 9.765230 6.651910 -0.121647
H 9.485603 6.934446 0.900757
H 9.966266 7.550479 -0.706152
H 10.662405 6.020676 -0.098855
C 7.242315 2.311149 0.515900
H 8.622582 2.505727 2.170432
H 5.973478 2.450414 -1.235474
Si 3.755968 0.125550 0.536176
Cl 2.980576 0.522445 -1.354791
Cl 3.412387 1.779741 1.744599
Cl 5.098772 -2.888924 1.655898
H 3.232429 -1.145497 0.984900

Table B.8 Transition State of Pathway D




Beginning E: -3509.894746
TS E: -3509.891800
Ending E: -3509.900792

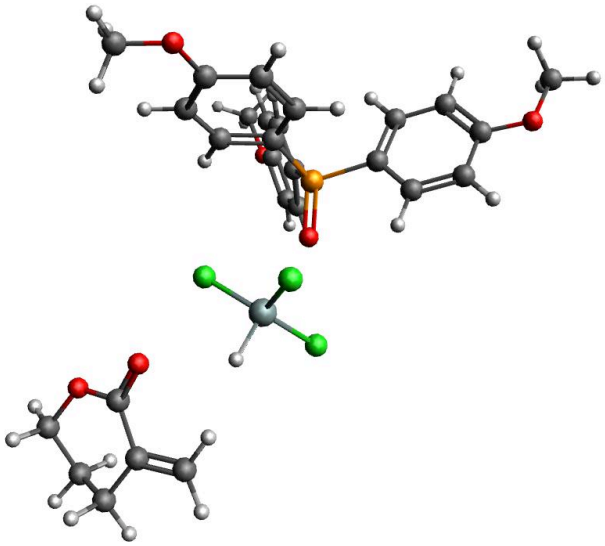
TS-D

68

C -4.065846 -0.652801 0.524318
C -2.599173 -1.008580 0.404165
C -4.399595 0.522960 -0.398803
C -2.121872 -2.253864 0.542039
O -2.067771 1.319378 -0.214092
H -5.435500 0.855122 -0.256118
H -4.287910 0.229767 -1.450954
C -3.461980 1.675752 -0.080189
H -3.621030 2.031115 0.947470
H -3.595069 2.522117 -0.758672
C -1.605156 0.073862 0.073851
O -0.410629 -0.122315 0.012239
H -1.060270 -2.453455 0.437904
H -4.293183 -0.362287 1.561885
H -4.685936 -1.527932 0.299163
H -2.783795 -3.090619 0.754400
P 6.874692 1.329923 -0.847673
O 5.641030 0.716296 -0.217749
C 6.561819 2.655322 -2.062276
C 7.912501 2.053713 0.465671
C 7.635111 -1.287765 -1.336190
C 8.750765 0.330676 -2.740840
C 9.465439 -0.694291 -3.370019
C 8.336571 -2.313974 -1.954810
C 9.255579 -2.023352 -2.976377
H 10.161856 -0.447002 -4.163741
H 8.182301 -3.350649 -1.671813
O 9.886770 -3.097436 -3.528953
C 6.826863 4.007512 -1.777350
C 5.976755 2.337950 -3.297017
C 5.675010 3.328985 -4.233612
C 6.533053 5.003490 -2.700615
H 7.266004 4.287800 -0.824940
H 5.724609 1.307188 -3.530936
C 5.957162 4.670545 -3.936519
H 5.214755 3.045057 -5.173312
O 5.707921 5.715235 -4.774397
H 6.736288 6.047856 -2.484207
C 7.283127 2.394536 1.677410
C 9.287189 2.279582 0.334527
H 6.220633 2.204077 1.795799
C 8.008854 2.955845 2.720270
C 9.386263 3.183458 2.577200
C 10.029670 2.842480 1.377732

H 11.094679 3.000185 1.249846
H 9.801934 2.010726 -0.584402
H 7.529386 3.218309 3.658379
O 10.009662 3.734008 3.657666
C 11.407792 3.987515 3.591557
H 11.674305 4.419262 4.557929
H 11.645417 4.702791 2.793521
H 11.974482 3.059956 3.437088
C 5.088049 5.454649 -6.029166
H 4.976271 6.427909 -6.509652
H 4.100034 4.995386 -5.896886
H 5.714977 4.806853 -6.655219
C 10.819332 -2.877225 -4.580813
H 10.338376 -2.404013 -5.446634
H 11.184443 -3.866098 -4.862975
H 11.660864 -2.258409 -4.242684
C 7.834978 0.052386 -1.720260
H 8.906929 1.354056 -3.072375
H 6.908862 -1.516244 -0.561775
Si 3.228467 0.232971 -0.082817
Cl 4.018320 -1.131086 1.280968
Cl 3.556850 -0.221719 -2.099339
Cl 3.252259 2.241320 0.480886
H 1.800490 -0.051093 0.008642

Table B.9 Additional Transition State of Pathway D



Beginning E: -3509.895419
TS E: -3509.892685
Ending E: -3509.899706

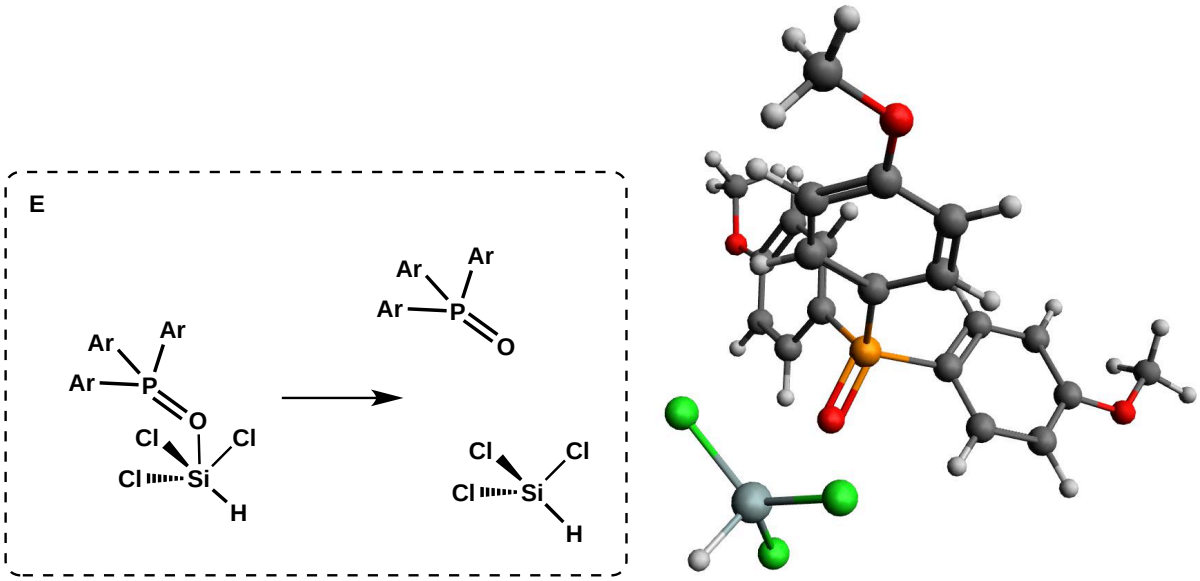
TS-D

68

C -2.323180 0.162026 -1.785906
C -1.199453 0.166527 -0.773362
C -1.983383 1.084692 -2.959218
C -0.840389 -0.911143 -0.061115
O -0.608012 2.462179 -1.440174
H -2.822650 1.156273 -3.662240
H -1.119603 0.693991 -3.512357
C -1.668523 2.470353 -2.419172
H -2.555706 2.916455 -1.948836
H -1.316742 3.148527 -3.200811
C -0.422558 1.438456 -0.560348
O 0.391147 1.588277 0.323582
H -0.031632 -0.867173 0.660658
H -3.249026 0.520202 -1.309461
H -2.519691 -0.861266 -2.125235
H -1.350493 -1.863632 -0.187026
P 7.271607 1.109252 0.331663
O 6.051477 0.249977 0.048866
C 6.975806 2.543654 1.417271
C 8.543736 0.083504 1.142646
C 7.714593 1.052814 -2.403817
C 8.783754 2.902864 -1.279518
C 9.322511 3.342145 -2.493407
C 8.244178 1.477930 -3.614782
C 9.053029 2.625264 -3.667101
H 9.931441 4.239406 -2.509585
H 8.036528 0.943701 -4.537213
O 9.518776 2.965393 -4.901869
C 7.338018 2.526154 2.777539
C 6.275723 3.656731 0.930025
C 5.943007 4.726116 1.763539
C 7.012094 3.583320 3.618460
H 7.873492 1.674540 3.186408
H 5.966410 3.693337 -0.110449
C 6.307353 4.688465 3.117560
H 5.401620 5.570542 1.351009
O 6.022139 5.669656 4.017732
H 7.283761 3.569248 4.669702
C 8.127387 -1.081851 1.813218
C 9.907332 0.397313 1.124398
H 7.074469 -1.348430 1.813574
C 9.050446 -1.897374 2.456314
C 10.415831 -1.569481 2.436602
C 10.846519 -0.416121 1.765083

H 11.896236 -0.147799 1.726814
H 10.259606 1.281164 0.599039
H 8.737713 -2.799991 2.972935
O 11.243453 -2.434297 3.089489
C 12.643315 -2.179669 3.083991
H 13.094338 -2.998434 3.646857
H 12.876638 -1.226126 3.575195
H 13.041778 -2.174833 2.061284
C 5.244220 6.783876 3.591196
H 5.111222 7.406162 4.477503
H 4.264786 6.461163 3.217297
H 5.765574 7.359052 2.815321
C 10.324018 4.130985 -5.033933
H 9.774522 5.030005 -4.726258
H 10.570826 4.200461 -6.094478
H 11.248048 4.045196 -4.447884
C 7.980846 1.758478 -1.215102
H 8.985574 3.480904 -0.381036
H 7.072916 0.176854 -2.369971
Si 3.595131 -0.032937 -0.004768
Cl 4.218502 -1.700527 -1.083711
Cl 3.733866 1.766117 -1.036795
Cl 3.953839 -0.047914 2.049351
H 2.143003 -0.240968 0.023945

Table B.10 Transition State of Pathway E



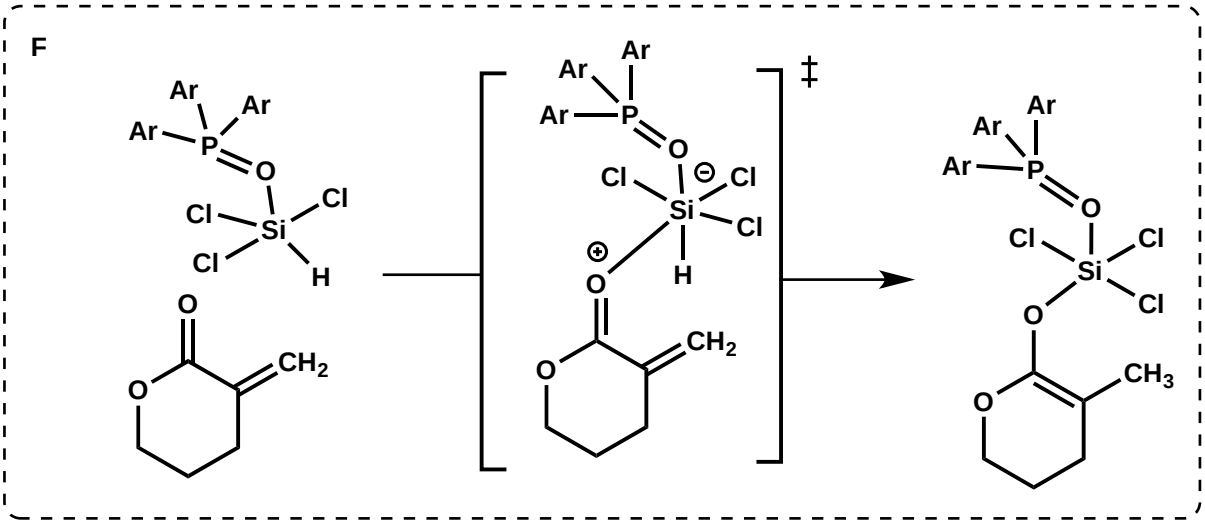

Starting E: -3125.997832
TS E: -3125.992291
Ending E: -3125.997151

TS-E
52

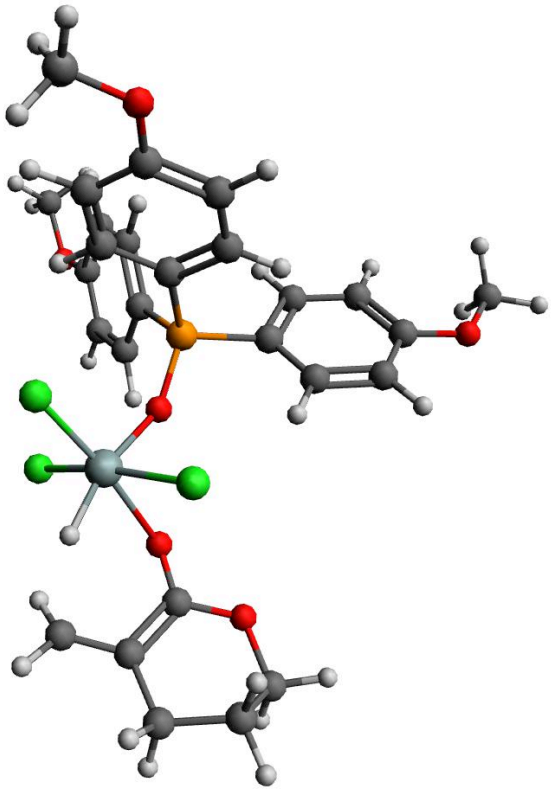
P -0.186168 0.026120 -0.165753
O 0.112160 0.277235 -1.637276
C 1.087126 0.630523 0.988400
C -1.746695 0.854295 0.276504
C -0.822057 -2.564708 -0.913620
C -0.163339 -2.349273 1.400065
C -0.364613 -3.719504 1.595312
C -1.027363 -3.924795 -0.731977
C -0.798487 -4.512169 0.523970
H -0.172378 -4.149844 2.571812
H -1.353986 -4.558000 -1.551435
O -1.019305 -5.854023 0.597150
C 0.896366 1.785589 1.769436
C 2.331426 -0.013912 1.045847
C 3.359435 0.464789 1.858611
C 1.911343 2.272872 2.583152
H -0.053509 2.310879 1.741705
H 2.514583 -0.896929 0.440253
C 3.151240 1.616355 2.632063
H 4.309334 -0.057725 1.872018
O 4.083043 2.167733 3.456474
H 1.768392 3.165055 3.185407
C -2.157524 1.952530 -0.502875
C -2.553453 0.449000 1.345905
H -1.552811 2.261856 -1.350369
C -3.334180 2.629971 -0.208812
C -4.134085 2.217705 0.870085
C -3.741381 1.120068 1.650125
H -4.347855 0.775346 2.479966
H -2.269293 -0.406854 1.952679
H -3.660340 3.475073 -0.807584
O -5.271220 2.939699 1.074937
C -6.146565 2.558401 2.130508
H -6.977808 3.264139 2.093070
H -5.649293 2.630369 3.106528
H -6.525159 1.538676 1.983712
C 5.377581 1.577283 3.520290
H 5.947207 2.192238 4.218630
H 5.866707 1.589043 2.538117
H 5.326715 0.547247 3.895610
C -0.774727 -6.525330 1.828045
H 0.276165 -6.429780 2.129631
H -1.006285 -7.575148 1.641849

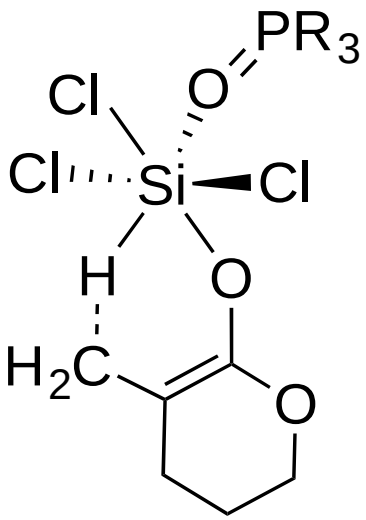
H -1.424370 -6.143937 2.626304
C -0.387671 -1.754166 0.153301
H 0.188920 -1.751819 2.237219
H -0.982598 -2.119644 -1.891350
Si 1.617235 0.772024 -3.478087
Cl -0.126139 0.287552 -4.499403
Cl 2.682355 -0.813635 -2.636265
Cl 1.674553 2.606238 -2.492353
H 2.505755 1.080517 -4.614244

Table B.11 Transition State of Pathway F with 4-OMe-TPPO catalyst.




Starting E: -3509.894673
TS E: -3509.875774
Ending E: -3509.932148





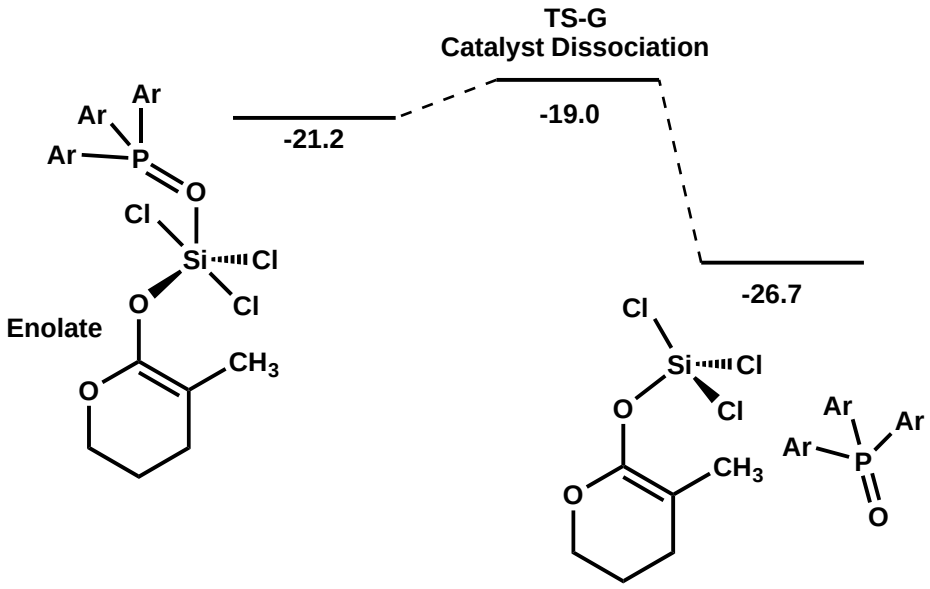

TS-F
68

C -0.263364 0.416974 -1.684215
C 0.802089 0.306745 -0.608210
C -0.042817 1.635086 -2.583096
C 1.090446 -0.862412 0.013127
O 1.438384 2.638418 -0.898708
H -0.939020 1.844105 -3.180068
H 0.784536 1.462651 -3.283972
C 0.260598 2.843761 -1.710662
H -0.582552 3.077898 -1.047472
H 0.497969 3.730629 -2.300128
C 1.679983 1.445798 -0.329624
O 2.719984 1.354356 0.343750
H 1.577342 -0.904051 0.982930
H -1.234144 0.521497 -1.181264
H -0.315747 -0.511145 -2.267689
H 0.627133 -1.784204 -0.335025
P 6.915652 1.615542 0.366054
O 5.419382 1.162716 0.321326
C 8.090180 0.690864 -0.648683
C 6.943110 3.337420 -0.186722
C 6.546482 1.782410 3.107777

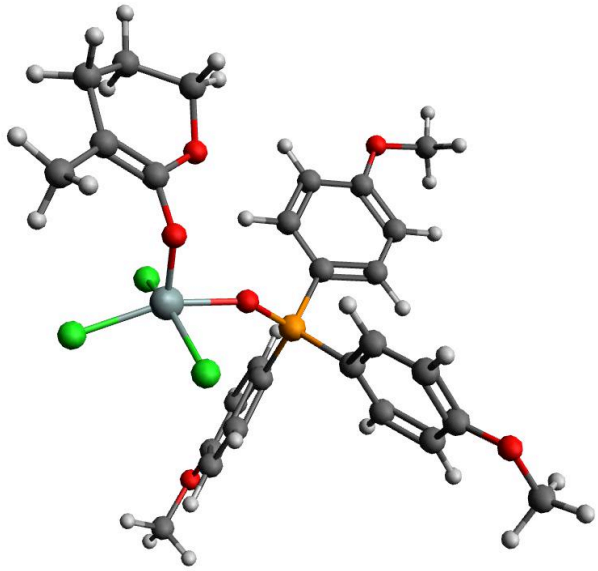
C 8.825158 1.324702 2.426126
C 9.236213 1.342045 3.762400
C 6.946623 1.798526 4.434404
C 8.293797 1.581692 4.771195
H 10.281222 1.157222 3.997501
H 6.229692 1.961617 5.230156
O 8.579775 1.602236 6.098445
C 8.564436 1.204889 -1.871777
C 8.518083 -0.584060 -0.247300
C 9.407619 -1.321731 -1.022413
C 9.445610 0.474635 -2.655869
H 8.245629 2.182722 -2.214813
H 8.150396 -1.019358 0.673937
C 9.873302 -0.795679 -2.237677
H 9.700768 -2.309193 -0.685085
O 10.730373 -1.436424 -3.074459
H 9.813387 0.867406 -3.598072
C 6.201388 3.731771 -1.319559
C 7.816983 4.257329 0.409226
H 5.504057 3.037434 -1.779722
C 6.339229 5.016971 -1.828953
C 7.211008 5.935697 -1.217173
C 7.948253 5.555451 -0.088633
H 8.619162 6.249676 0.405377
H 8.394956 3.976594 1.285049
H 5.792512 5.344172 -2.706942
O 7.278271 7.160671 -1.800454
C 8.114457 8.155709 -1.217928
H 7.991478 9.044847 -1.837442
H 9.168961 7.844836 -1.233800
H 7.807873 8.378230 -0.189693
C 11.162078 -2.752268 -2.742098
H 11.818345 -3.058044 -3.558319
H 10.311217 -3.441722 -2.676880
H 11.721395 -2.760200 -1.798824
C 9.911985 1.330087 6.519784
H 10.228606 0.326123 6.205681
H 9.892398 1.379762 7.609819
H 10.613217 2.079002 6.131668
C 7.484297 1.542817 2.081116
H 9.567669 1.134248 1.656130
H 5.498701 1.925552 2.861479
Si 4.274605 -0.168294 -0.041709
Cl 4.038963 -0.529081 2.165439
Cl 5.627662 -1.823137 -0.381984
Cl 4.230567 0.558893 -2.199389

H 3.033463 -0.942479 -0.310610

Table B.12 Transition State of Pathway G




Starting E: -3509.932842
TS E: -3509.929339
Ending E: -3509.941645



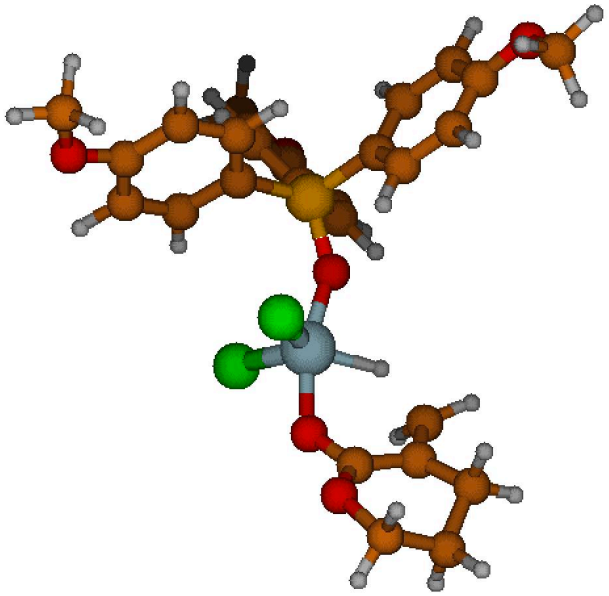
TS-G
68

C -6.282245 -0.792223 -0.971423
C -5.185423 0.197424 -1.311271
C -5.757973 -1.948684 -0.110659
C -5.578410 1.502812 -1.966138
O -3.448700 -1.309343 -0.563788

H -6.451459 -2.799522 -0.122413
H -5.646115 -1.625420 0.932535
C -4.394442 -2.383839 -0.633125
H -4.468074 -2.717421 -1.680074
H -3.956284 -3.190874 -0.038254
C -3.902835 -0.108281 -1.049428
O -2.859446 0.713930 -1.331029
H -5.118452 1.619165 -2.956898
H -6.739057 -1.182758 -1.896303
H -7.091498 -0.268768 -0.440153
H -6.665868 1.541986 -2.098810
P 0.937153 0.038750 0.157242
O -0.457826 0.439922 -0.371889
C 1.485219 1.044746 1.556471
C 0.869277 -1.701377 0.646486
C 1.747168 0.012268 -2.498097
C 3.502990 0.501315 -0.905786
C 4.435320 0.579530 -1.944781
C 2.664390 0.085810 -3.535029
C 4.015407 0.367896 -3.265601
H 5.468161 0.811998 -1.713776
H 2.357111 -0.056080 -4.566059
O 4.834130 0.421232 -4.349804
C 1.721518 0.493132 2.828314
C 1.630778 2.429416 1.379053
C 2.000681 3.253184 2.441171
C 2.095697 1.304332 3.890916
H 1.604848 -0.574107 2.988930
H 1.442228 2.878926 0.406982
C 2.232506 2.690094 3.706063
H 2.093794 4.318583 2.274906
O 2.589513 3.399417 4.808079
H 2.274498 0.889951 4.878134
C -0.341327 -2.231162 1.135879
C 1.986368 -2.540078 0.541720
H -1.224860 -1.602879 1.187613
C -0.415035 -3.560746 1.526829
C 0.712736 -4.393255 1.430115
C 1.919463 -3.879092 0.933262
H 2.799216 -4.505716 0.836120
H 2.924650 -2.160167 0.146036
H -1.343371 -3.981452 1.901405
O 0.533579 -5.679785 1.833347
C 1.627550 -6.587917 1.748508
H 1.246875 -7.541322 2.116977
H 2.464410 -6.259847 2.377419

H 1.966304 -6.704581 0.711224
C 2.688246 4.818834 4.714263
H 2.948884 5.160846 5.716657
H 1.731603 5.261610 4.411497
H 3.475638 5.115501 4.010003
C 6.213863 0.719768 -4.158802
H 6.346131 1.712843 -3.710714
H 6.657577 0.708094 -5.155265
H 6.701065 -0.037882 -3.531683
C 2.158303 0.213956 -1.165312
H 3.837105 0.679497 0.112378
H 0.702409 -0.181282 -2.715583
Si -1.899539 1.659747 -0.351193
Cl -0.684851 2.691098 -1.817530
Cl -3.037169 3.435558 0.068088
Cl -2.137302 0.955470 1.691900
H -5.286514 2.376971 -1.375060

Table B.13 Continued SE-GSM from pathway C (-Cl) (then Zstruct)



Free Energy: -3049.451679

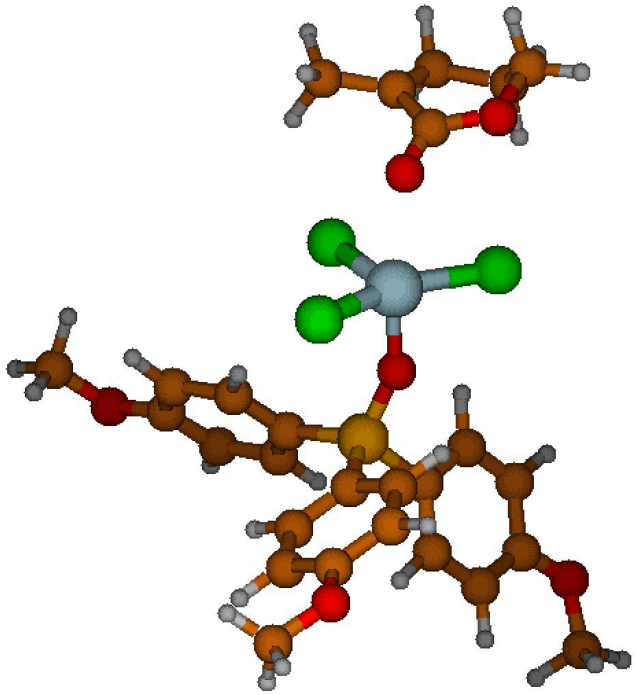
67

C -0.550793 -0.760877 1.427950
C 0.691216 -0.490917 0.608220
C -1.727387 -0.179559 0.625056
C 1.857865 -1.290714 0.551104
O -0.174431 1.664545 -0.068794
H -2.675631 -0.311620 1.157813

H -1.812021 -0.711985 -0.329737
C -1.525434 1.312989 0.377153
H -1.689266 1.895649 1.288409
H -2.181528 1.693851 -0.408521
C 0.778563 0.742108 -0.039157
O 1.911087 1.135625 -0.545878
H 2.270802 -1.576224 -0.417092
H -0.505115 -0.281550 2.418826
H -0.688151 -1.833342 1.594794
H 1.980429 -2.061257 1.313432
P 6.409269 1.026988 1.737639
O 4.961855 0.613948 1.200399
C 6.398157 0.661693 3.497206
C 7.606627 0.000545 0.882145
C 6.803028 3.247927 0.120833
C 6.939067 3.669547 2.503878
C 7.108465 5.031844 2.257970
C 6.956176 4.597883 -0.131330
C 7.097614 5.507284 0.936584
H 7.238746 5.708550 3.094525
H 6.961553 4.980550 -1.147290
O 7.220251 6.803142 0.586441
C 7.440999 -0.074032 4.094700
C 5.341142 1.119000 4.301078
C 5.317533 0.858078 5.669786
C 7.425610 -0.338143 5.456034
H 8.263662 -0.447037 3.492431
H 4.522730 1.681826 3.859857
C 6.365163 0.125824 6.256577
H 4.486607 1.221195 6.263949
O 6.442113 -0.185595 7.567372
H 8.220824 -0.907927 5.925881
C 7.277865 -1.333189 0.557518
C 8.888011 0.478943 0.571464
H 6.288230 -1.720759 0.783936
C 8.202561 -2.154964 -0.062990
C 9.488014 -1.667146 -0.374800
C 9.827278 -0.342764 -0.052626
H 10.806831 0.057087 -0.286052
H 9.163640 1.502467 0.807202
H 7.958446 -3.180300 -0.325080
O 10.312653 -2.543855 -0.981987
C 11.631441 -2.129186 -1.355486
H 12.085176 -2.999044 -1.829725
H 12.216610 -1.843078 -0.473966
H 11.592453 -1.297391 -2.069467

C 5.412247 0.250547 8.458176
H 5.704512 -0.116990 9.441362
H 4.442736 -0.179330 8.177119
H 5.348779 1.344962 8.477588
C 7.354830 7.799010 1.604793
H 6.476019 7.807935 2.260810
H 7.426806 8.747847 1.074229
H 8.264684 7.635995 2.193946
C 6.768433 2.761085 1.447683
H 6.940801 3.320263 3.532033
H 6.695664 2.567434 -0.717946
Si 3.564726 1.089196 0.241067
Cl 4.477854 1.098337 -1.621586
Cl 3.252568 2.912636 1.214166
H 2.978894 -0.396657 0.694926

Table B.14 Continued SE-GSM from pathway B (then Zstruct)



Free Energy: -3509.854210

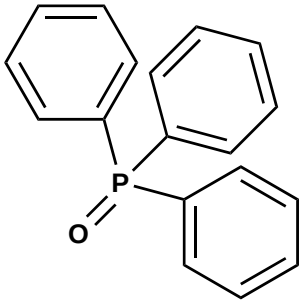
68

C 5.860324 0.029330 -2.226674
C 5.633353 0.751055 -0.928265
C 5.989368 -1.484027 -2.007846
C 5.505142 2.240848 -0.918502
O 5.945187 -1.245713 0.387270
H 6.455816 -1.971071 -2.873118

H 5.022286 -1.965563 -1.824398
C 6.768760 -1.694137 -0.712430
H 7.716258 -1.133564 -0.702638
H 6.974329 -2.744764 -0.499232
C 5.342108 -0.023221 0.251831
O 4.552479 0.337179 1.136612
H 5.781190 2.665940 0.052161
H 6.766688 0.420734 -2.719737
H 5.013639 0.282333 -2.886916
H 6.144413 2.671223 -1.699856
P -1.248708 -0.290022 0.300344
O 0.281385 -0.583694 0.261923
C -1.694719 1.190802 -0.623456
C -2.039741 -1.744101 -0.430574
C -1.295933 -0.987021 2.986860
C -2.808923 0.796045 2.365080
C -3.280422 0.864190 3.679353
C -1.759138 -0.929761 4.290435
C -2.757709 -0.004418 4.646498
H -4.039280 1.596464 3.930587
H -1.351762 -1.580313 5.058584
O -3.142733 -0.027361 5.948890
C -2.549818 1.131352 -1.740739
C -1.142376 2.428121 -0.252545
C -1.443447 3.585207 -0.968019
C -2.852197 2.279863 -2.458735
H -2.977239 0.183220 -2.052326
H -0.459758 2.491627 0.590329
C -2.303093 3.514835 -2.075740
H -0.992837 4.523039 -0.663904
O -2.656928 4.579246 -2.840672
H -3.505817 2.244962 -3.324780
C -1.410767 -2.458883 -1.467494
C -3.258087 -2.200589 0.086467
H -0.441063 -2.140192 -1.839493
C -2.008856 -3.597494 -1.986701
C -3.237648 -4.049927 -1.471564
C -3.860017 -3.352621 -0.425411
H -4.792969 -3.698098 0.003932
H -3.746716 -1.665724 0.894484
H -1.534255 -4.166462 -2.780347
O -3.731281 -5.181285 -2.038762
C -4.959923 -5.717565 -1.555424
H -5.139536 -6.617116 -2.145808
H -5.785428 -5.010766 -1.703479
H -4.885383 -5.985377 -0.493758

C -2.098336 5.857822 -2.545636
H -2.505139 6.534812 -3.297870
H -1.004809 5.837745 -2.621413
H -2.395901 6.198596 -1.546352
C -4.108348 0.917384 6.402229
H -3.744762 1.944518 6.275304
H -4.247068 0.707921 7.463998
H -5.063394 0.793092 5.876730
C -1.820367 -0.125410 2.002755
H -3.218124 1.477836 1.625819
H -0.506611 -1.688492 2.733461
Si 1.984590 -0.091441 0.473251
Cl 2.618771 -2.089451 -0.365631
Cl 1.482023 1.310715 2.173301
Cl 2.141636 1.199579 -1.235023
H 4.474679 2.561538 -1.127224

Table B.15 TPPO catalyst



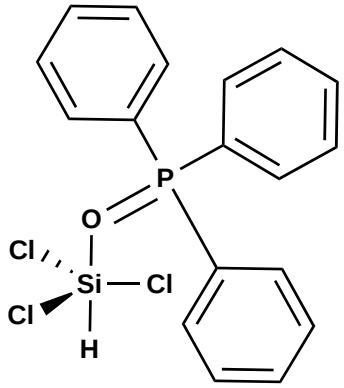

Free Energy: -1111.58120039956

35

| | | | |
|---|---|---|---|
| P | 6.81561064 | 1.15843923 | 0.65276035 |
| O | 5.67995017 | 0.17609321 | 0.78091720 |
| C | 7.95103067 | 0.73558560 | -0.72411819 |
| C | 6.23585837 | 2.86798319 | 0.32746826 |
| C | 7.20984451 | 0.95264723 | 3.38730841 |
| C | 9.21249925 | 1.55363772 | 2.16232402 |
| C | 9.93051736 | 1.59848914 | 3.36055254 |
| C | 7.92909233 | 1.00000154 | 4.58331565 |
| C | 9.28908784 | 1.32537545 | 4.57181997 |
| H | 10.99089541 | 1.83815298 | 3.34578279 |
| H | 7.42985210 | 0.77567812 | 5.52256085 |
| H | 9.84933751 | 1.35820665 | 5.50296183 |
| C | 8.69008095 | 1.68894727 | -1.44018621 |
| C | 8.06120283 | -0.62132392 | -1.06635782 |
| C | 8.91260204 | -1.01894362 | -2.09932818 |
| C | 9.54197224 | 1.28825333 | -2.47337485 |

| | | | |
|---|---|---|---|
| H | 8.59187141 | 2.74612330 | -1.20676845 |
| H | 7.46384874 | -1.35453015 | -0.53125251 |
| C | 9.65616188 | -0.06546708 | -2.80165542 |
| H | 8.98963555 | -2.07143415 | -2.36028623 |
| H | 10.31570980 | -0.37549208 | -3.60844793 |
| H | 10.10833903 | 2.03393939 | -3.02581111 |
| C | 5.06666890 | 3.00914230 | -0.43723969 |
| C | 6.89065299 | 4.01438962 | 0.80095543 |
| H | 4.54195460 | 2.12076405 | -0.77818177 |
| C | 4.57319602 | 4.27937625 | -0.74041827 |
| C | 5.23803911 | 5.41920016 | -0.27709754 |
| C | 6.39414275 | 5.28536200 | 0.49641944 |
| H | 6.90583898 | 6.16843200 | 0.87111566 |
| H | 7.77922969 | 3.92042516 | 1.41974710 |
| H | 3.66639202 | 4.37902266 | -1.33166699 |
| H | 4.85168639 | 6.40808065 | -0.51117156 |
| C | 7.84527468 | 1.23885640 | 2.16851647 |
| H | 9.72500642 | 1.74972068 | 1.22416821 |
| H | 6.15868684 | 0.67749570 | 3.38758855 |

Table B.16 TPPO catalyst bound to trichlorosilane.



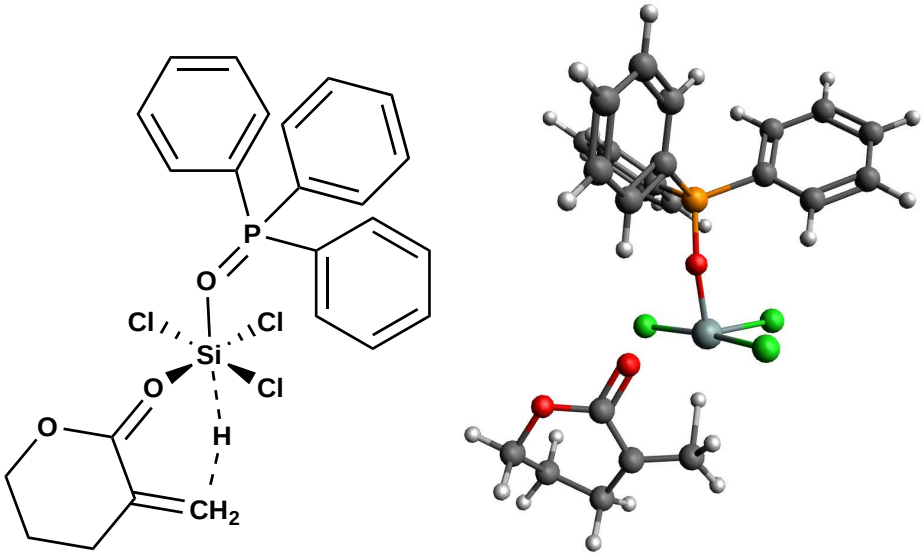

Free Energy: -2782.41123544620

40

| | | | |
|---|---|---|---|
| P | -0.52055559 | -0.24298168 | -0.05205312 |
| O | 0.34975497 | -1.06322040 | 0.92388850 |
| C | -2.30965545 | -0.32647543 | 0.25001874 |
| C | 0.01593922 | 1.48541461 | 0.10465581 |
| C | 1.02480239 | -1.41695780 | -2.03210646 |
| C | -1.14653868 | -0.61184168 | -2.77205085 |
| C | -0.84787690 | -1.01287897 | -4.07575342 |
| C | 1.31511799 | -1.81649192 | -3.33718743 |
| C | 0.38226028 | -1.61321692 | -4.35841426 |
| H | -1.57983972 | -0.86564484 | -4.86521231 |
| H | 2.26566872 | -2.29649824 | -3.55305272 |

| | | | |
|---|---|---|---|
| H | 0.61036239 | -1.92900044 | -5.37293688 |
| C | -3.00656513 | 0.78198508 | 0.75572953 |
| C | -2.99327978 | -1.53221110 | 0.01239686 |
| C | -4.35920139 | -1.62038864 | 0.27711138 |
| C | -4.37479793 | 0.68644120 | 1.01631469 |
| H | -2.48672019 | 1.71451063 | 0.95113604 |
| H | -2.45956313 | -2.40131084 | -0.35936257 |
| C | -5.05040159 | -0.51274107 | 0.77881443 |
| H | -4.88155665 | -2.55651667 | 0.09959068 |
| H | -6.11432091 | -0.58683568 | 0.98835827 |
| H | -4.90794422 | 1.54669425 | 1.41179546 |
| C | 0.60288783 | 1.90247700 | 1.30939790 |
| C | -0.16479420 | 2.40280277 | -0.94231313 |
| H | 0.76416809 | 1.18810579 | 2.11015431 |
| C | 0.98704134 | 3.23602444 | 1.46714088 |
| C | 0.79467443 | 4.15107140 | 0.42877402 |
| C | 0.22401766 | 3.73301069 | -0.77772931 |
| H | 0.08833132 | 4.43949495 | -1.59210769 |
| H | -0.59435469 | 2.08245144 | -1.88777853 |
| H | 1.44101665 | 3.55509808 | 2.40117661 |
| H | 1.09637960 | 5.18753668 | 0.55540975 |
| C | -0.20806050 | -0.80832192 | -1.74721302 |
| H | -2.11184352 | -0.16307232 | -2.55383653 |
| H | 1.74088086 | -1.59133034 | -1.23468329 |
| Si | 0.55246636 | -2.40021415 | 2.21808135 |
| Cl | -0.16908086 | -3.81456843 | 0.76006760 |
| H | 0.73251813 | -3.45530073 | 3.23891830 |
| Cl | -0.81839160 | -1.29677516 | 3.45086748 |
| Cl | 2.61717439 | -1.86030364 | 2.21507293 |

Table B.17 Transition State of Pathway F with TPPO catalyst.



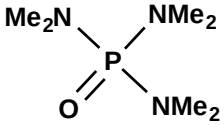

Transition state energy: -3166.282138

56

C 1.665823 -4.622710 -0.825015
C 1.995664 -3.359196 -0.058312
C 1.987254 -4.437567 -2.311708
C 2.354282 -3.346412 1.295917
O 2.057332 -1.997152 -2.069167
H 1.552189 -5.242232 -2.917114
H 3.071874 -4.440188 -2.475457
C 1.423565 -3.095714 -2.761145
H 0.339880 -3.043201 -2.584646
H 1.613858 -2.895593 -3.818883
C 2.334086 -2.146177 -0.748282
O 2.996413 -1.220226 -0.212988
H 2.144322 -2.447104 1.869213
H 0.594127 -4.855074 -0.721278
H 2.208298 -5.476633 -0.396632
H 2.364374 -4.273456 1.869983
P 6.646063 0.801828 0.560336
O 5.462707 -0.167621 0.835480
C 7.767410 0.301201 -0.769916
C 5.834002 2.362871 0.123105
C 6.997317 0.879639 3.313358
C 8.983302 1.382769 1.998262
C 9.701485 1.610334 3.173355
C 7.729271 1.092715 4.482165
C 9.074742 1.466152 4.414105
H 10.750403 1.887042 3.117567

H 7.246723 0.956432 5.445267
H 9.638512 1.634159 5.329025
C 7.885560 1.064077 -1.942003
C 8.540424 -0.862566 -0.607897
C 9.419424 -1.253755 -1.615636
C 8.772483 0.666758 -2.945110
H 7.286598 1.960016 -2.073005
H 8.445018 -1.468397 0.288391
C 9.536888 -0.490804 -2.782291
H 10.003953 -2.160477 -1.493605
H 10.223047 -0.801883 -3.565659
H 8.860306 1.259321 -3.851390
C 4.491022 2.329900 -0.286634
C 6.520906 3.584920 0.196865
H 3.952836 1.386865 -0.326383
C 3.848436 3.522171 -0.628571
C 4.533512 4.738062 -0.562043
C 5.869517 4.769582 -0.148542
H 6.400811 5.714613 -0.085090
H 7.554005 3.619364 0.534739
H 2.808052 3.495116 -0.939552
H 4.026057 5.663206 -0.824186
C 7.627965 1.019691 2.065493
H 9.484526 1.473007 1.038144
H 5.953670 0.583615 3.372985
Si 4.806498 -1.762124 1.172815
Cl 3.637127 -0.747708 2.815443
Cl 6.322283 -2.558153 2.477898
Cl 5.643234 -2.666929 -0.681087
H 3.719380 -2.935264 1.155110

Table B.18 HMPA catalyst.



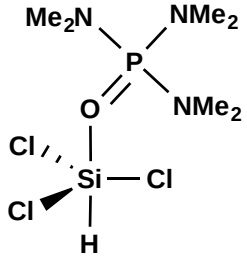

Free Energy: -820.357474610977

29

| | | | |
|---|---|---|---|
| P | 6.64992443 | 1.10500928 | 0.35065106 |
| O | 5.50318254 | 0.15613969 | 0.51238685 |
| N | 7.49218682 | 1.15982662 | -1.12207298 |
| N | 6.10582820 | 2.70431271 | 0.48748401 |
| N | 7.88808856 | 0.71606773 | 1.43611689 |
| C | 9.14180604 | 1.45426220 | 1.52927628 |
| C | 7.58014676 | -0.08836936 | 2.61764142 |

| | | | |
|---|---|---|---|
| C | 4.88138257 | 2.95431936 | 1.24950691 |
| C | 7.00554084 | 3.85131489 | 0.42909298 |
| C | 6.78697355 | 1.70109871 | -2.29119831 |
| C | 8.31276440 | -0.00397548 | -1.47850479 |
| H | 6.66380775 | -0.65538060 | 2.44849119 |
| H | 7.45596673 | 0.53633128 | 3.51720690 |
| H | 8.40358425 | -0.79203002 | 2.80408743 |
| H | 9.36151219 | 1.95930319 | 0.58623685 |
| H | 9.96408975 | 0.75544248 | 1.74018931 |
| H | 9.12554651 | 2.20436721 | 2.33676672 |
| H | 8.84653465 | -0.37510730 | -0.60239556 |
| H | 9.04620829 | 0.29719135 | -2.23685228 |
| H | 7.70469592 | -0.82445690 | -1.89042142 |
| H | 7.84407118 | 3.64679728 | -0.23999712 |
| H | 7.40261452 | 4.12711133 | 1.42016853 |
| H | 6.45909092 | 4.71937313 | 0.03575744 |
| H | 6.19250220 | 2.57038244 | -2.00641083 |
| H | 6.11832567 | 0.95446799 | -2.74728178 |
| H | 7.52551200 | 2.00824975 | -3.04251921 |
| H | 4.23635678 | 2.07601833 | 1.20511835 |
| H | 4.35141209 | 3.80944227 | 0.80919425 |
| H | 5.09286393 | 3.19038047 | 2.30576091 |

Table B.19 HMPA catalyst bound to trichlorosilane.



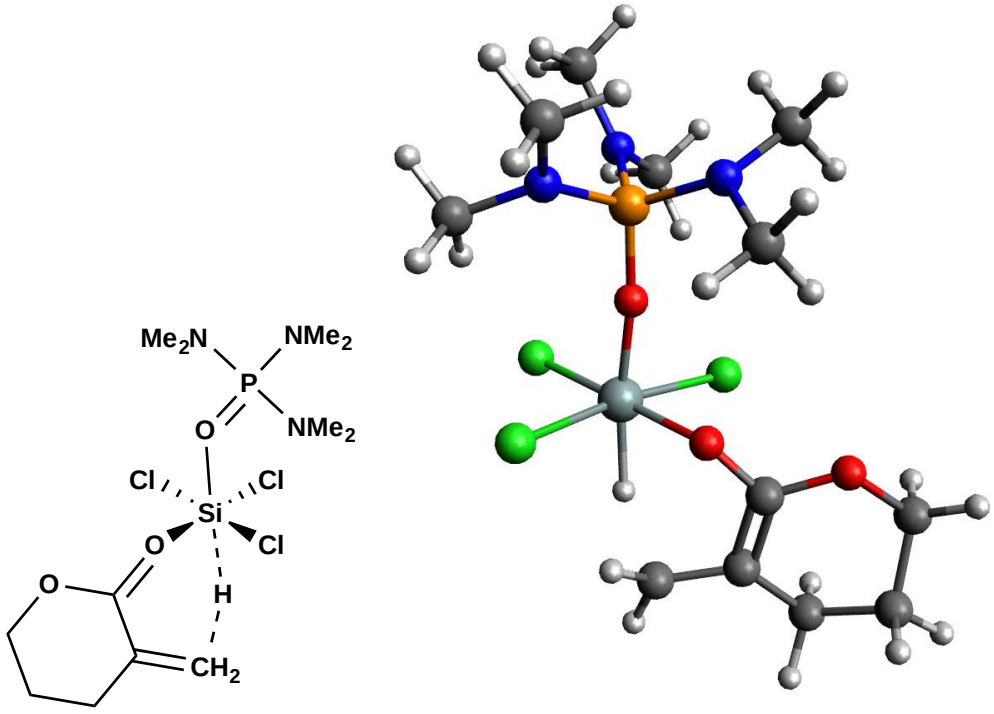

Free Energy: -2491.18593788665

34

| | | | |
|---|---|---|---|
| P | -0.65509351 | -0.15337079 | 0.03004191 |
| O | 0.22607402 | -0.65891614 | 1.21411686 |
| N | -2.22971635 | -0.68047285 | 0.12004453 |
| N | -0.55334057 | 1.49232983 | 0.13945777 |
| N | -0.05770244 | -0.60122098 | -1.43990080 |
| Si | 0.66742383 | -1.90314317 | 2.34108016 |
| Cl | 0.97380738 | -3.33366053 | 0.54924725 |
| H | -0.21065261 | -2.94489271 | 2.89067689 |
| Cl | -0.00449120 | -0.53646108 | 3.99553349 |
| Cl | 2.69662429 | -1.79894398 | 2.79258070 |
| C | -3.25847943 | 0.16741215 | 0.74085571 |

| | | | |
|---|---|---|---|
| H | -4.22395303 | -0.05748848 | 0.27408199 |
| H | -3.03580834 | 1.22266980 | 0.57982058 |
| H | -3.33525753 | -0.01875733 | 1.82086361 |
| C | -2.51770887 | -2.12200815 | 0.24877347 |
| H | -1.67834183 | -2.72629041 | -0.09846445 |
| H | -3.40582141 | -2.36624391 | -0.34618166 |
| H | -2.71103452 | -2.38317531 | 1.29763966 |
| C | -0.34684142 | 2.20322252 | 1.41097441 |
| H | 0.45378939 | 2.94039512 | 1.27608383 |
| H | -0.05921253 | 1.50939992 | 2.20120962 |
| H | -1.26195442 | 2.73084126 | 1.71340976 |
| C | -0.90433243 | 2.35583386 | -0.99029901 |
| H | -0.92637354 | 1.78315492 | -1.91959010 |
| H | -0.14902319 | 3.14498401 | -1.08617846 |
| H | -1.88395754 | 2.83317878 | -0.84071467 |
| C | -0.76118314 | -1.42326288 | -2.42767617 |
| H | -0.48372287 | -1.07455411 | -3.42945721 |
| H | -1.84057404 | -1.31726689 | -2.31305387 |
| H | -0.48369495 | -2.48085709 | -2.33309993 |
| C | 1.40240010 | -0.53577990 | -1.63433517 |
| H | 1.85558928 | 0.14401380 | -0.90906789 |
| H | 1.60500213 | -0.15474575 | -2.64191028 |
| H | 1.85221134 | -1.52615353 | -1.50823252 |

Table B.20 Transition State of Pathway F with HMPA catalyst.



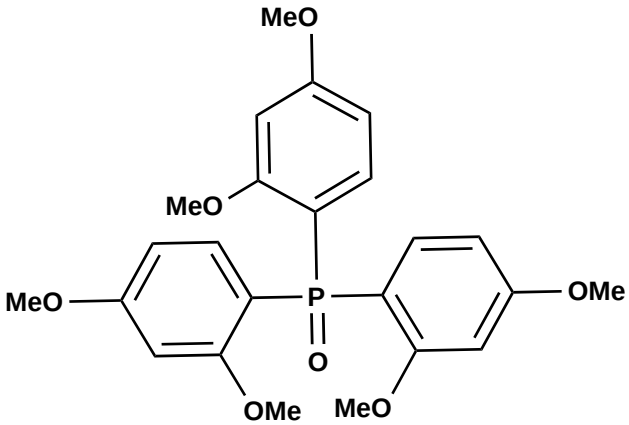

TS Energy: -2875.066034

50

C 3.836225 -6.057246 -1.333665
C 4.746827 -5.189789 -0.492923
C 4.413332 -6.132829 -2.754931
C 4.846345 -5.213025 0.898392
O 5.557019 -3.962768 -2.426163
H 3.722274 -6.645189 -3.435844
H 5.354295 -6.697365 -2.752121
C 4.663093 -4.725076 -3.277102
H 3.724331 -4.158935 -3.336558
H 5.143195 -4.719368 -4.258244
C 5.471936 -4.136283 -1.095584
O 6.051860 -3.244765 -0.389586
H 5.787836 -4.964780 1.379974
H 2.818847 -5.638255 -1.374700
H 3.751177 -7.059561 -0.898749
H 4.183318 -5.855517 1.478186
P 6.702162 0.462026 0.213785
O 6.012624 -0.875686 0.501044
N 7.283958 0.482812 -1.346623
N 5.639220 1.703148 0.473287
N 8.016236 0.656846 1.194798
Si 5.126113 -2.290208 1.046324
Cl 4.068542 -1.249330 2.647690
Cl 6.840057 -2.896736 2.366302
Cl 3.443796 -1.947073 -0.458038
H 4.443231 -3.716273 1.320779
C 9.325858 1.150495 0.776709
C 7.874997 0.452013 2.644348
C 4.208179 1.607532 0.150429
C 6.080683 3.040727 0.866173
C 6.635205 1.264704 -2.401316
C 7.974749 -0.723738 -1.839113
H 6.877968 0.086438 2.894169
H 8.054715 1.398605 3.174142
H 8.596496 -0.297806 2.985305
H 9.336715 1.346234 -0.295990
H 10.100487 0.408873 1.012433
H 9.568438 2.081465 1.309640
H 8.418327 -1.278363 -1.009777
H 8.771378 -0.421442 -2.529940
H 7.277724 -1.396087 -2.353885
H 7.121057 3.024908 1.196449
H 5.458610 3.396249 1.696817

H 5.984452 3.754182 0.033950
H 6.203229 2.179173 -1.990120
H 5.845243 0.693659 -2.910402
H 7.389777 1.549637 -3.144745
H 3.933661 0.589567 -0.127585
H 3.956877 2.286994 -0.676975
H 3.619412 1.886588 1.031687

Table B.21 2,4-diOMe-TPPO catalyst.



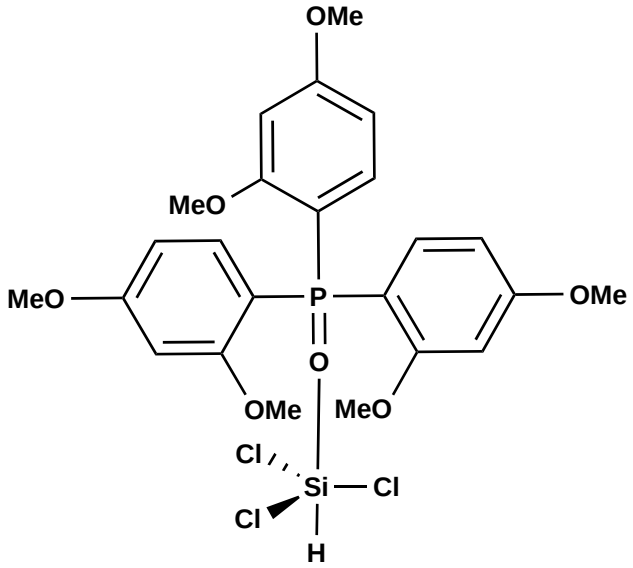

Free Energy: -1798.73535143058

59

| | | | |
|---|---|---|---|
| P | 6.95193244 | 1.04146263 | 0.01302502 |
| O | 5.81746538 | 0.15046327 | -0.42133164 |
| C | 8.38689355 | 0.93188018 | -1.12820099 |
| C | 6.40865590 | 2.79485406 | -0.00086679 |
| C | 6.70608822 | 0.69371207 | 2.80647626 |
| C | 8.94040298 | 0.46480987 | 1.95011829 |
| C | 9.43073126 | 0.17269941 | 3.22781854 |
| C | 7.17053096 | 0.39817855 | 4.08892078 |
| C | 8.53183943 | 0.13244486 | 4.29696570 |
| H | 10.48810793 | -0.02135424 | 3.36467419 |
| H | 6.50927052 | 0.36797833 | 4.94619919 |
| C | 8.81046069 | 2.01949396 | -1.89299053 |
| C | 8.98548468 | -0.32708962 | -1.39673814 |
| C | 9.96488389 | -0.45959813 | -2.38038501 |
| C | 9.79323938 | 1.91097459 | -2.88395699 |
| H | 8.35445204 | 2.99019090 | -1.73064700 |
| O | 8.55585495 | -1.36418011 | -0.63233541 |
| C | 10.36891879 | 0.66062843 | -3.12305838 |
| H | 10.43481259 | -1.41113707 | -2.59863091 |
| O | 11.33491634 | 0.41634696 | -4.05685914 |
| H | 10.08024739 | 2.78826617 | -3.45153468 |
| C | 5.12531626 | 3.03003423 | -0.49776513 |

| | | | |
|---|---|---|---|
| C | 7.13473505 | 3.89916255 | 0.50387908 |
| H | 4.56081575 | 2.17681023 | -0.86399780 |
| C | 4.55115503 | 4.30547570 | -0.51796810 |
| C | 5.28796655 | 5.38016714 | -0.01243830 |
| C | 6.57941895 | 5.17895547 | 0.50100735 |
| H | 7.11389852 | 6.04060281 | 0.88242395 |
| O | 8.39058920 | 3.63487365 | 0.96808270 |
| H | 3.55057277 | 4.43727186 | -0.91261894 |
| O | 4.84625327 | 6.67233641 | 0.02988388 |
| C | 7.59257984 | 0.71694857 | 1.70018502 |
| H | 9.64575389 | 0.49933832 | 1.12638002 |
| O | 5.40729115 | 0.99084187 | 2.53923890 |
| O | 8.87689799 | -0.15030828 | 5.58934169 |
| C | 4.44635374 | 0.92841631 | 3.58250931 |
| C | 9.14609787 | 4.68226636 | 1.56086551 |
| C | 8.97873791 | -2.68480274 | -0.94060377 |
| H | 8.43332184 | -3.33384305 | -0.25386279 |
| H | 10.05857410 | -2.80669695 | -0.78178194 |
| H | 8.72533122 | -2.94853845 | -1.97511489 |
| H | 4.67080869 | 1.65272023 | 4.37677208 |
| H | 4.38908893 | -0.08139151 | 4.00897492 |
| H | 3.49268796 | 1.18100963 | 3.11617724 |
| H | 9.36341305 | 5.47795525 | 0.83610995 |
| H | 10.08034077 | 4.22234239 | 1.88756972 |
| H | 8.62415491 | 5.10705284 | 2.42800155 |
| C | 10.23725536 | -0.44494399 | 5.87860020 |
| C | 11.79692395 | 1.49835522 | -4.85612040 |
| C | 3.55377835 | 6.96533601 | -0.48789539 |
| H | 3.42208385 | 8.04132760 | -0.36065040 |
| H | 2.77129333 | 6.43283785 | 0.06786796 |
| H | 3.48546903 | 6.71052386 | -1.55317467 |
| H | 12.55950599 | 1.07605714 | -5.51278244 |
| H | 12.24260989 | 2.28815627 | -4.23769348 |
| H | 10.98490851 | 1.92057526 | -5.46222784 |
| H | 10.27431608 | -0.64990863 | 6.95005049 |
| H | 10.88847543 | 0.40814303 | 5.64699832 |
| H | 10.58037570 | -1.32819554 | 5.32443405 |

Table B.22 2,4-diOMe-TPPO catalyst bound to trichlorosilane.



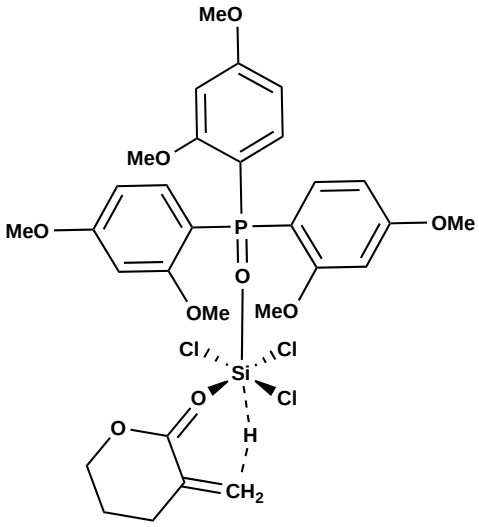

Free Energy: -3469.56994092534

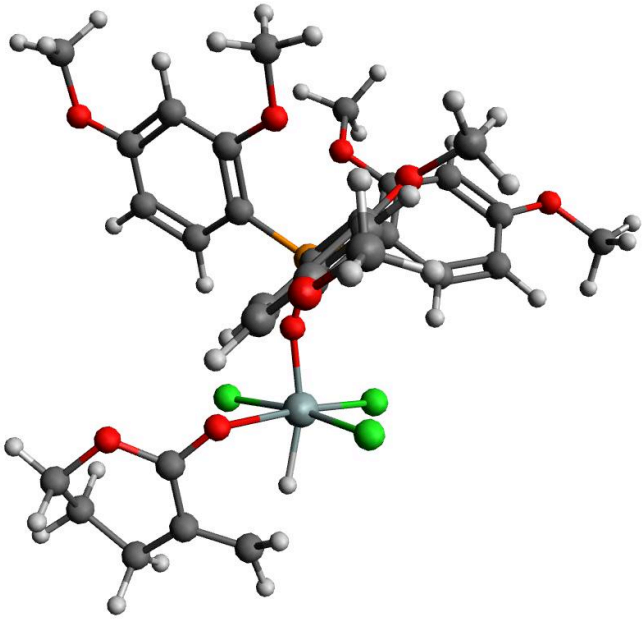
64

| | | | |
|---|---|---|---|
| P | 7.37833018 | 1.30119809 | -0.17620990 |
| O | 6.05847561 | 0.70799793 | -0.74610951 |
| C | 8.85952587 | 0.55723550 | -0.88572928 |
| C | 7.23025549 | 3.09435499 | -0.42338817 |
| C | 6.30288155 | 0.17355182 | 2.12833697 |
| C | 8.29716022 | 1.47791031 | 2.50801920 |
| C | 8.20857032 | 1.21762986 | 3.87229908 |
| C | 6.19529154 | -0.09523786 | 3.49448958 |
| C | 7.15516103 | 0.42902206 | 4.36620834 |
| H | 8.92962829 | 1.60829197 | 4.57992614 |
| H | 5.36989088 | -0.70004476 | 3.84966815 |
| O | 7.16312400 | 0.23750132 | 5.71280656 |
| C | 9.19669066 | 0.76198146 | -2.24011316 |
| C | 9.63415066 | -0.34288608 | -0.13725002 |
| C | 10.71194227 | -1.01582588 | -0.69306293 |
| C | 10.27408554 | 0.08110852 | -2.82147671 |
| O | 8.43045648 | 1.64852420 | -2.91648850 |
| H | 9.37511085 | -0.53607464 | 0.89830581 |
| C | 11.02848890 | -0.80718713 | -2.04324360 |
| H | 11.29950246 | -1.72029453 | -0.11395031 |
| O | 12.09070435 | -1.51155462 | -2.51908689 |
| H | 10.51230755 | 0.24324384 | -3.86337236 |
| C | 5.91891947 | 3.60289542 | -0.36858427 |
| C | 8.28676451 | 4.00252364 | -0.64046467 |
| H | 5.09329027 | 2.91316051 | -0.22542940 |
| C | 5.64572269 | 4.95402065 | -0.51617352 |

| | | | |
|---|---|---|---|
| C | 6.70519403 | 5.84347050 | -0.73562043 |
| C | 8.02262646 | 5.37228304 | -0.80119445 |
| H | 8.83747744 | 6.06069762 | -0.97496161 |
| O | 9.54891905 | 3.49873631 | -0.69099254 |
| H | 4.62952840 | 5.33177075 | -0.47975320 |
| O | 6.36358935 | 7.15411540 | -0.87732545 |
| C | 7.34078524 | 0.95103542 | 1.60611356 |
| O | 9.28221198 | 2.22842395 | 1.94605383 |
| H | 5.54943959 | -0.22500719 | 1.45961430 |
| C | 10.29411951 | 2.78351684 | 2.77763154 |
| C | 10.63332936 | 4.34883624 | -1.03210801 |
| C | 8.52838250 | 1.74041930 | -4.33456237 |
| H | 10.85845236 | 1.99576219 | 3.29213268 |
| H | 9.86664164 | 3.47464826 | 3.51481533 |
| H | 10.95810753 | 3.32847136 | 2.10536564 |
| H | 7.73706109 | 2.42695029 | -4.63531848 |
| H | 8.35670917 | 0.76378051 | -4.80068759 |
| H | 9.50452796 | 2.14153000 | -4.63763334 |
| H | 10.49249844 | 4.80056205 | -2.02279435 |
| H | 11.51514490 | 3.70578106 | -1.04858032 |
| H | 10.77530440 | 5.14061143 | -0.28433702 |
| Si | 5.01223104 | -0.46920841 | -1.68036769 |
| H | 4.14655243 | -1.43434822 | -2.39617064 |
| Cl | 3.42457036 | 0.05692490 | -0.31942766 |
| Cl | 6.41721210 | -2.03634425 | -1.18220543 |
| Cl | 5.24490235 | 0.74541978 | -3.43482091 |
| C | 6.12658476 | -0.55029107 | 6.29596463 |
| H | 6.34026260 | -0.56984560 | 7.36558395 |
| H | 6.13739503 | -1.57270998 | 5.89933084 |
| H | 5.14274055 | -0.09663045 | 6.12498399 |
| C | 12.44115702 | -1.39719318 | -3.89443161 |
| H | 13.30061822 | -2.05466465 | -4.03393468 |
| H | 12.72443628 | -0.36759995 | -4.14895034 |
| H | 11.61923663 | -1.72725938 | -4.54194031 |
| C | 7.38112985 | 8.11435692 | -1.13401246 |
| H | 6.86769294 | 9.07380868 | -1.21344024 |
| H | 7.90168469 | 7.89964500 | -2.07638895 |
| H | 8.10724108 | 8.15640793 | -0.31149681 |

Table B.23 Transition State of Pathway F with 2,4-diOMe-TPPO catalyst.



TS E: -3853.446083

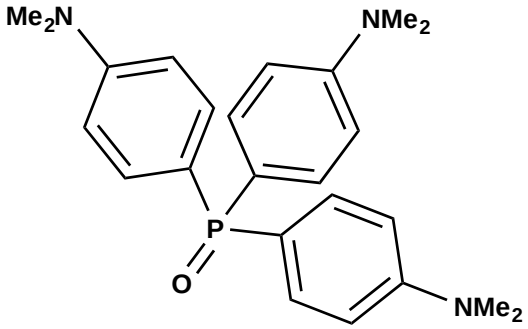
80

C -0.044404 0.662216 -0.380130
C 1.277839 0.283279 0.259982
C -0.087682 2.168394 -0.673072
C 1.776387 -1.010276 0.308355
O 1.898383 2.590351 0.688226
H -1.115842 2.506277 -0.849985
H 0.502405 2.399024 -1.567808
C 0.502674 2.927537 0.509033
H -0.033267 2.699695 1.441383
H 0.501198 4.009870 0.358763
C 2.235434 1.287704 0.592540
O 3.458923 1.013511 0.717614
H 3.052185 -0.943360 -0.613933
H -0.874957 0.395821 0.291640
H -0.192801 0.086949 -1.303801
H 2.488461 -1.294327 1.079090
P 7.111088 1.575963 -0.328332
O 5.725199 0.972188 -0.726793
C 8.373571 0.607638 -1.184761
C 6.966086 3.306978 -0.827764
C 6.152023 1.753017 2.227754
C 8.518708 1.252744 2.162939
C 8.538817 1.225434 3.565939

C 6.166302 1.749150 3.613461
C 7.363794 1.473258 4.285746
H 9.465654 1.022714 4.084477
H 5.261151 1.927720 4.185665
O 7.298700 1.473593 5.646279
C 9.237289 1.072982 -2.205405
C 8.417064 -0.749972 -0.845619
C 9.283857 -1.644337 -1.466972
C 10.115417 0.188248 -2.832554
O 9.155580 2.386413 -2.544120
H 7.738312 -1.132180 -0.087397
C 10.136972 -1.166430 -2.469002
H 9.258150 -2.689365 -1.185222
O 11.021751 -1.935598 -3.161203
H 10.781039 0.511741 -3.621988
C 5.859401 3.713479 -1.589721
C 7.902826 4.277107 -0.424328
H 5.122372 2.976219 -1.894367
C 5.680220 5.044892 -1.940948
C 6.612126 6.001611 -1.522424
C 7.730381 5.624512 -0.762462
H 8.450798 6.362588 -0.439197
O 8.962736 3.815461 0.291433
H 4.820188 5.359219 -2.523484
O 6.357221 7.287393 -1.898861
C 7.241945 8.322120 -1.488078
H 6.823436 9.245346 -1.892906
H 8.250408 8.171632 -1.894766
H 7.291617 8.393684 -0.393917
C 11.042973 -3.339223 -2.915839
H 11.794146 -3.744169 -3.595719
H 10.067441 -3.791892 -3.131846
H 11.331005 -3.557492 -1.879713
C 8.465532 1.163023 6.397094
H 8.827683 0.152890 6.167563
H 8.164019 1.211938 7.444339
H 9.264680 1.893466 6.213733
C 7.312714 1.498074 1.471649
O 9.646684 1.068160 1.424795
H 5.208768 1.924007 1.717461
Si 4.447389 -0.211431 -0.818894
Cl 5.231748 -1.408042 0.909405
Cl 5.257506 -1.521333 -2.327943
Cl 3.348138 1.080138 -2.324768
H 1.189380 -1.827427 -0.109929
C 10.835485 0.608955 2.056146

C 9.934640 4.726489 0.780768
C 9.908405 2.868835 -3.649863
H 10.667930 -0.344134 2.575046
H 11.229064 1.350625 2.764310
H 11.555491 0.463239 1.251421
H 9.621971 3.915510 -3.762187
H 9.660040 2.320762 -4.566909
H 10.986339 2.800270 -3.457834
H 10.449917 5.239106 -0.042564
H 10.651867 4.118870 1.334560
H 9.483915 5.466225 1.454499

Table B.24 4-$NMe_2$-TPPO catalyst.



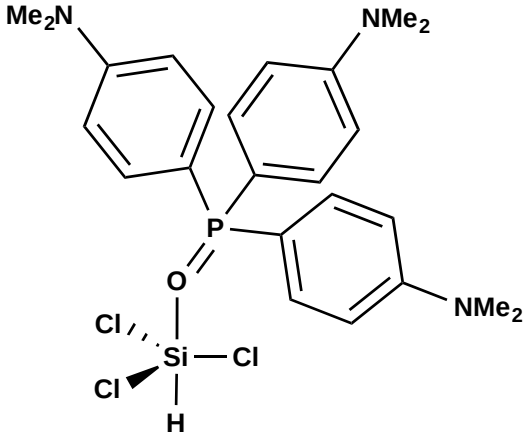

Free Energy: -1513.49795728210

59

| | | | |
|---|---|---|---|
| P | 6.62640384 | 1.31289678 | 0.17475548 |
| O | 5.36236656 | 0.51349697 | -0.03622095 |
| C | 7.90252517 | 0.93122852 | -1.07353872 |
| C | 6.33127146 | 3.11174539 | 0.08226470 |
| C | 6.54183537 | 0.58205811 | 2.85052254 |
| C | 8.75423611 | 1.09971372 | 2.07604205 |
| C | 9.26833036 | 0.83945047 | 3.34433261 |
| C | 7.03981306 | 0.31491484 | 4.12140473 |
| C | 8.42005641 | 0.45234062 | 4.41004997 |
| H | 10.33782393 | 0.92919050 | 3.49551264 |
| H | 6.34653109 | -0.01018818 | 4.88829845 |
| N | 8.91937923 | 0.21810529 | 5.68466230 |
| C | 8.84827586 | 1.85162735 | -1.54508291 |
| C | 7.92642867 | -0.36396940 | -1.61416781 |
| C | 8.86571597 | -0.73506921 | -2.56991365 |
| C | 9.79777253 | 1.49518182 | -2.50066829 |
| H | 8.83704365 | 2.87604258 | -1.18081431 |
| H | 7.17862574 | -1.08528714 | -1.29463729 |
| C | 9.84228590 | 0.18278691 | -3.02994480 |
| H | 8.82889677 | -1.74363002 | -2.96487876 |

| | | | |
|---|---|---|---|
| N | 10.80304708 | -0.19357403 | -3.96060931 |
| H | 10.49609982 | 2.25102429 | -2.84097651 |
| C | 5.30168247 | 3.56527048 | -0.75741958 |
| C | 7.06222232 | 4.07347004 | 0.79321556 |
| H | 4.70567198 | 2.83930499 | -1.30435710 |
| C | 5.01723186 | 4.91979068 | -0.89272451 |
| C | 5.75145082 | 5.89620654 | -0.17547283 |
| C | 6.79197245 | 5.43424349 | 0.66645865 |
| H | 7.38744554 | 6.13433557 | 1.24092067 |
| H | 7.85424255 | 3.76398913 | 1.47094507 |
| H | 4.21094489 | 5.21354023 | -1.55450668 |
| N | 5.45032081 | 7.24852707 | -0.27743307 |
| C | 7.38342882 | 0.98895290 | 1.80368834 |
| H | 9.44755087 | 1.37465558 | 1.28439232 |
| H | 5.48057429 | 0.45149098 | 2.65535126 |
| C | 10.35836092 | 0.13386256 | 5.88126811 |
| C | 8.06113167 | -0.40182772 | 6.68295548 |
| C | 4.52834976 | 7.69901883 | -1.30895769 |
| C | 6.37053528 | 8.22678372 | 0.28102162 |
| C | 11.62449607 | 0.82835376 | -4.59095302 |
| C | 10.65902646 | -1.46418046 | -4.65551824 |
| H | 10.84926032 | 1.07104744 | 5.59383534 |
| H | 10.81905961 | -0.68610407 | 5.30547925 |
| H | 10.56451712 | -0.03264367 | 6.94060300 |
| H | 7.72328390 | -1.40899643 | 6.38750740 |
| H | 7.17433720 | 0.21331933 | 6.87493215 |
| H | 8.61198921 | -0.48589670 | 7.62204965 |
| H | 9.73106495 | -1.52204007 | -5.24830728 |
| H | 10.66536460 | -2.30066455 | -3.94739087 |
| H | 11.50720472 | -1.59747255 | -5.33019622 |
| H | 6.49058241 | 8.08153344 | 1.36094409 |
| H | 5.96175894 | 9.22786284 | 0.12858418 |
| H | 7.36946900 | 8.18528527 | -0.18458185 |
| H | 12.19031349 | 1.39267207 | -3.84103305 |
| H | 11.03278128 | 1.54366999 | -5.18660966 |
| H | 12.34718973 | 0.34483043 | -5.25162848 |
| H | 3.54809392 | 7.22275171 | -1.19406462 |
| H | 4.89490278 | 7.49129024 | -2.32822163 |
| H | 4.38208242 | 8.77673073 | -1.20938791 |

Table B.25 4-$NMe_2$-TPPO catalyst bound to trichlorosilane.



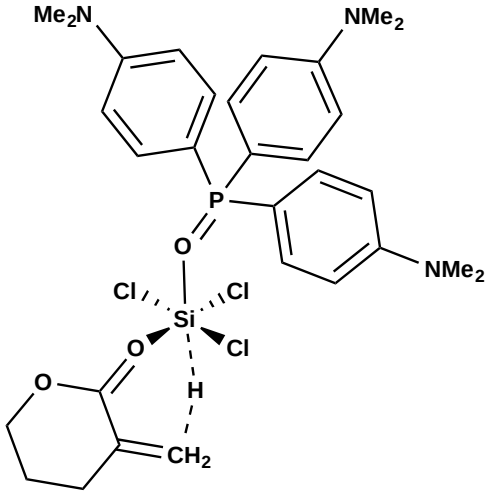

Free Energy: -3184.33522848818

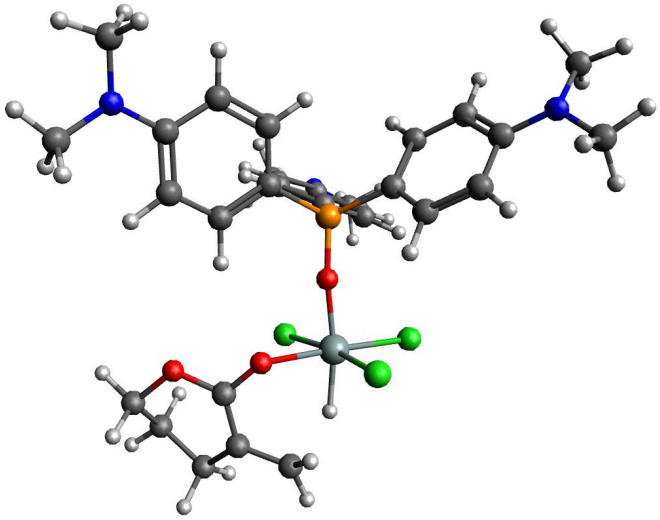
64

| | | | |
|---|---|---|---|
| P | 6.89342057 | 1.58119170 | -0.29035090 |
| O | 5.51951395 | 0.89333667 | -0.62718194 |
| C | 8.21398757 | 1.13780711 | -1.41406620 |
| C | 6.61269358 | 3.35837137 | -0.31851775 |
| C | 6.35357263 | 0.41346402 | 2.17947450 |
| C | 8.60017591 | 1.24669845 | 1.90793967 |
| C | 8.90273435 | 0.88506166 | 3.21422487 |
| C | 6.64601678 | 0.04662658 | 3.48627326 |
| C | 7.92645458 | 0.27957176 | 4.04858224 |
| H | 9.90659965 | 1.06376720 | 3.58109324 |
| H | 5.87105037 | -0.44169499 | 4.06450776 |
| N | 8.21510087 | -0.07250475 | 5.34982130 |
| C | 8.52886059 | 1.93979922 | -2.52591578 |
| C | 8.89593696 | -0.08474239 | -1.26142857 |
| C | 9.86650701 | -0.48260591 | -2.16722237 |
| C | 9.50562472 | 1.55712032 | -3.43181415 |
| H | 7.98885892 | 2.86622645 | -2.69369382 |
| H | 8.65510103 | -0.74274195 | -0.43068150 |
| C | 10.21024421 | 0.33421245 | -3.27748531 |
| H | 10.35493508 | -1.43673902 | -2.01113170 |
| N | 11.18744647 | -0.04799676 | -4.16652716 |
| H | 9.70170255 | 2.20383628 | -4.27832705 |
| C | 5.34493394 | 3.87675571 | -0.62772707 |
| C | 7.63558537 | 4.26018325 | 0.02140142 |
| H | 4.54061292 | 3.20931383 | -0.91498092 |
| C | 5.10460988 | 5.24374650 | -0.59277920 |
| C | 6.12582346 | 6.16190204 | -0.24214038 |
| C | 7.40818083 | 5.62903084 | 0.05613502 |
| H | 8.23060171 | 6.28441396 | 0.31720730 |

| | | | |
|---|---|---|---|
| H | 8.63319054 | 3.89748636 | 0.25719446 |
| H | 4.11254323 | 5.59405263 | -0.85054991 |
| N | 5.88258959 | 7.51698760 | -0.18955942 |
| C | 7.32291323 | 1.02411184 | 1.36589857 |
| H | 9.38606811 | 1.69162002 | 1.30200062 |
| H | 5.37233374 | 0.19128173 | 1.77350886 |
| C | 9.57104266 | 0.06791295 | 5.85785801 |
| C | 7.23692524 | -0.81030557 | 6.13731370 |
| C | 4.58070557 | 8.03918459 | -0.58033056 |
| C | 6.96342634 | 8.44434038 | 0.10436611 |
| C | 11.46470514 | 0.76396941 | -5.34372268 |
| C | 11.77489118 | -1.37809758 | -4.07457787 |
| H | 9.90941435 | 1.11081318 | 5.80523133 |
| H | 10.29074805 | -0.55612317 | 5.30529656 |
| H | 9.59196034 | -0.23593437 | 6.90578428 |
| H | 6.99926132 | -1.78877772 | 5.69336748 |
| H | 6.30339659 | -0.24332494 | 6.24147107 |
| H | 7.63829174 | -0.97670067 | 7.13856771 |
| H | 11.02167018 | -2.17026573 | -4.19606637 |
| H | 12.27921730 | -1.52493417 | -3.11115334 |
| H | 12.52160379 | -1.49348378 | -4.86141957 |
| H | 7.41181074 | 8.23823761 | 1.08529058 |
| H | 6.56618882 | 9.46031671 | 0.12753293 |
| H | 7.76073543 | 8.40788614 | -0.65343689 |
| H | 11.73465526 | 1.78897527 | -5.06055237 |
| H | 10.60659122 | 0.80936749 | -6.03145529 |
| H | 12.31231902 | 0.33344105 | -5.87937891 |
| H | 3.77854457 | 7.60934486 | 0.03334025 |
| H | 4.35312103 | 7.83474518 | -1.63720727 |
| H | 4.57055990 | 9.12035174 | -0.43231724 |
| Si | 4.66392472 | -0.09074480 | -1.77026978 |
| H | 5.27729653 | -1.01067423 | -2.73723921 |
| Cl | 4.68416951 | -1.77335870 | -0.25938519 |
| Cl | 4.92217531 | 1.54923181 | -3.35233868 |
| Cl | 2.60197326 | 0.23362533 | -1.60271076 |

Table B.26 Transition State of Pathway F with 4-$NMe_2$-TPPO catalyst.



TS E: -3568.218062

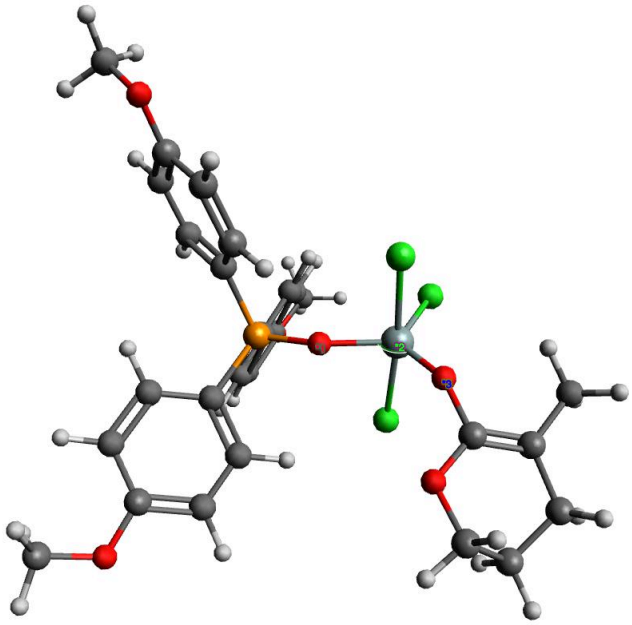
80

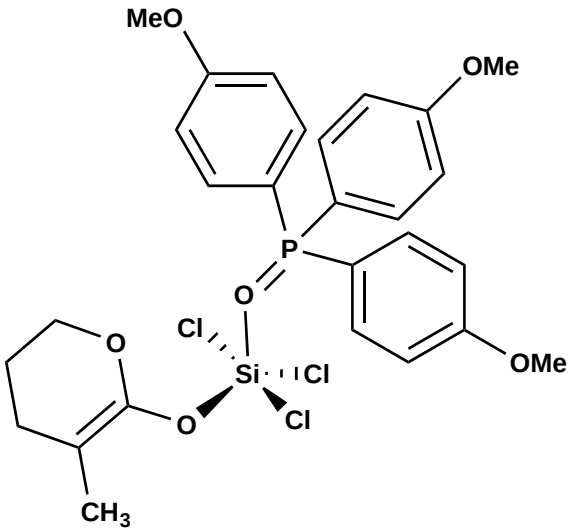
C 0.818315 0.071738 -2.504767
C 1.322305 0.554921 -1.155730
C 1.538492 0.809890 -3.639175
C 1.149458 -0.132462 0.035281
O 2.463672 2.470256 -2.102086
H 0.999590 0.697130 -4.587598
H 2.548540 0.405806 -3.773685
C 1.650169 2.288015 -3.287422
H 0.664184 2.737493 -3.101318
H 2.163751 2.867467 -4.057208
C 2.259447 1.621651 -1.084389
O 3.018750 1.779750 -0.077176
H 1.190882 0.388643 0.986371
H -0.264553 0.244207 -2.584460
H 0.971923 -1.011438 -2.594905
H 0.612685 -1.080597 0.039086
P 6.874209 1.736543 0.686012
O 5.376029 1.345901 0.845679
C 7.815954 0.717806 -0.453591
C 6.859401 3.441047 0.093477
C 6.852535 1.754508 3.461268
C 9.032540 1.481036 2.464484
C 9.615439 1.453652 3.726687
C 7.423832 1.722856 4.725494
C 8.824681 1.583687 4.897392
H 10.687313 1.314608 3.798064
H 6.767950 1.786756 5.584962

N 9.397750 1.574321 6.154513
C 8.201359 1.186395 -1.720886
C 8.142553 -0.606580 -0.109747
C 8.828335 -1.427661 -0.989966
C 8.889277 0.372222 -2.611474
H 7.952676 2.198847 -2.026042
H 7.829407 -1.014157 0.847446
C 9.223924 -0.962707 -2.271341
H 9.032998 -2.446449 -0.684910
N 9.909576 -1.779213 -3.148498
H 9.151721 0.777641 -3.581721
C 5.766108 3.917170 -0.647756
C 7.923057 4.320004 0.353160
H 4.909793 3.274384 -0.827114
C 5.745009 5.220520 -1.128384
C 6.822098 6.112364 -0.887770
C 7.913040 5.625244 -0.124399
H 8.751588 6.269834 0.113390
H 8.772665 3.993023 0.948216
H 4.872455 5.546339 -1.681963
N 6.806373 7.405385 -1.371138
C 7.877612 8.325301 -1.025517
H 7.701121 9.281914 -1.520025
H 8.851780 7.948641 -1.364669
H 7.938331 8.506417 0.058673
C 10.062311 -3.195696 -2.843717
H 10.630439 -3.672609 -3.644753
H 9.093418 -3.710103 -2.750570
H 10.619414 -3.339735 -1.910158
C 10.806167 1.237635 6.302218
H 11.035886 0.224663 5.936743
H 11.076610 1.290393 7.358870
H 11.441774 1.950159 5.760966
C 7.647091 1.640008 2.306865
H 9.670851 1.359013 1.593767
H 5.772516 1.835410 3.370760
Si 3.997177 0.275125 0.744187
Cl 3.179574 0.987227 2.679644
Cl 5.017349 -1.464278 1.627260
Cl 4.585438 -0.329926 -1.424236
H 2.711119 -0.585998 0.424309
C 8.547274 1.538236 7.336418
C 5.620762 7.914768 -2.044009
C 10.134427 -1.338778 -4.517896
H 10.710701 -2.100536 -5.046752
H 10.714250 -0.408480 -4.541236

H 9.193163 -1.173513 -5.064667
H 5.801461 8.945001 -2.355518
H 4.735757 7.903409 -1.389438
H 5.389228 7.328247 -2.942705
H 7.874352 2.403067 7.362538
H 9.175936 1.581593 8.227563
H 7.935897 0.623732 7.386995

Table B.27 120 degree enolate complex with 4-OMe-TPPO catalyst.






120° O-Si-O enolate free energy: -3509.93648943515

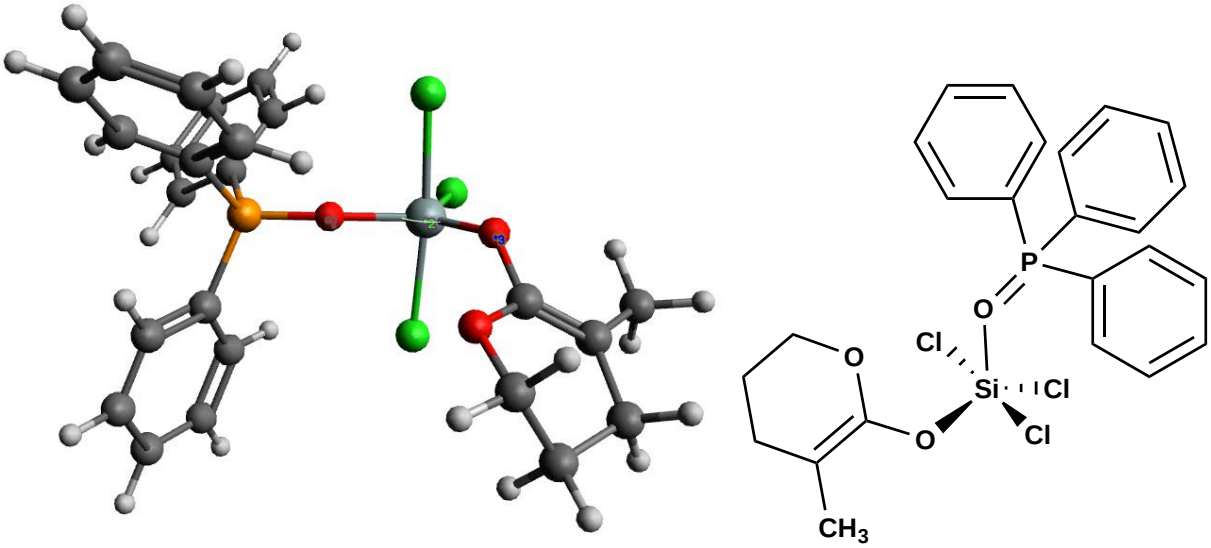
68

| | | | |
|---|---|---|---|
| C | 0.00698442 | 0.43531228 | -2.26628758 |
| C | 0.96568523 | -0.01706475 | -1.18529433 |
| C | 0.37609557 | 1.82625205 | -2.79915434 |
| C | 0.90750027 | -1.46186276 | -0.76956540 |
| O | 1.90776710 | 2.19254171 | -0.93611424 |
| H | -0.45844232 | 2.27912613 | -3.34947408 |
| H | 1.22782658 | 1.75193252 | -3.48710354 |
| C | 0.76979459 | 2.72078140 | -1.62969260 |
| H | -0.06213109 | 2.81101473 | -0.91422704 |
| H | 1.06935899 | 3.72289777 | -1.94899933 |
| C | 1.84185692 | 0.85487481 | -0.65676301 |
| O | 2.73384484 | 0.53650752 | 0.31627556 |
| H | 1.56260341 | -1.67573133 | 0.07863465 |
| H | -1.02707790 | 0.43536718 | -1.88217766 |
| H | 0.01707993 | -0.29430726 | -3.09021171 |
| H | -0.11753183 | -1.74333255 | -0.48331596 |

| | | | |
|---|---|---|---|
| P | 7.03211868 | 1.77793889 | 0.57487684 |
| O | 5.54522068 | 1.29737843 | 0.62525673 |
| C | 8.06626112 | 0.75356108 | -0.48358681 |
| C | 6.99751378 | 3.47232915 | -0.03511552 |
| C | 6.83992316 | 2.04750162 | 3.32941836 |
| C | 9.04469279 | 1.46692342 | 2.50742002 |
| C | 9.54495014 | 1.48480645 | 3.81164328 |
| C | 7.32942874 | 2.07073066 | 4.62514332 |
| C | 8.68372809 | 1.78689798 | 4.87713282 |
| H | 10.59070905 | 1.25396102 | 3.97982367 |
| H | 6.67593039 | 2.28401444 | 5.46544627 |
| O | 9.05729705 | 1.82267274 | 6.18136640 |
| C | 8.62209182 | 1.25156666 | -1.67784372 |
| C | 8.28272178 | -0.59072310 | -0.14079887 |
| C | 9.03129488 | -1.42658371 | -0.96570685 |
| C | 9.37841672 | 0.42865194 | -2.49914866 |
| H | 8.45555587 | 2.28394005 | -1.96918436 |
| H | 7.84995999 | -1.00499375 | 0.76548242 |
| C | 9.58444607 | -0.91753253 | -2.15109755 |
| H | 9.16264789 | -2.46505825 | -0.68537158 |
| O | 10.33137151 | -1.64496546 | -3.01888192 |
| H | 9.80674053 | 0.80053769 | -3.42478672 |
| C | 6.04335104 | 3.84746198 | -1.00284520 |
| C | 7.92213881 | 4.42036549 | 0.42082182 |
| H | 5.31173342 | 3.12425740 | -1.35346132 |
| C | 6.03746833 | 5.13957921 | -1.50760162 |
| C | 6.97737708 | 6.08392796 | -1.05725900 |
| C | 7.92141560 | 5.72160966 | -0.08430040 |
| H | 8.64347082 | 6.43615395 | 0.29401769 |
| H | 8.64989770 | 4.15503791 | 1.18324588 |
| H | 5.30620864 | 5.44392507 | -2.24999939 |
| O | 6.88971036 | 7.31788731 | -1.61671044 |
| C | 7.81908337 | 8.32304563 | -1.22004916 |
| H | 7.56446364 | 9.20545819 | -1.80816223 |
| H | 8.84938683 | 8.01873109 | -1.44298402 |
| H | 7.72253997 | 8.55342330 | -0.15186235 |
| C | 10.52120345 | -3.03720497 | -2.76980982 |
| H | 11.12877923 | -3.40254223 | -3.59857600 |
| H | 9.56209173 | -3.56822499 | -2.75428243 |
| H | 11.05290554 | -3.20256185 | -1.82481535 |
| C | 10.40247728 | 1.50330315 | 6.52581523 |
| H | 10.65160920 | 0.47594109 | 6.23182611 |
| H | 10.45597611 | 1.59650905 | 7.61117864 |
| H | 11.10829711 | 2.20448758 | 6.06313126 |
| C | 7.69597936 | 1.74492643 | 2.24974894 |
| H | 9.71954673 | 1.22060349 | 1.69242676 |

| | | | |
|---|---|---|---|
| H | 5.78448107 | 2.22776707 | 3.15394379 |
| Si | 4.33697752 | 0.07368880 | 0.32067428 |
| Cl | 4.18519714 | -0.18731534 | 2.51554254 |
| Cl | 4.94023337 | -1.94912010 | 0.06196537 |
| Cl | 4.63763925 | 0.46346892 | -1.88032812 |
| H | 1.19837185 | -2.12656811 | -1.59696942 |

Table B.28 120 degree enolate complex with TPPO catalyst.



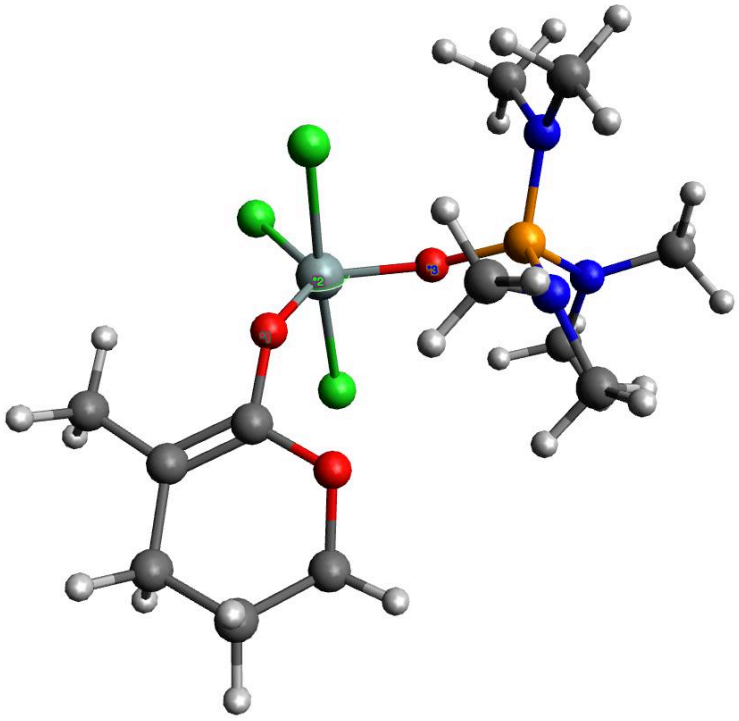

120° O-Si-O enolate free energy: -3166.34753564560

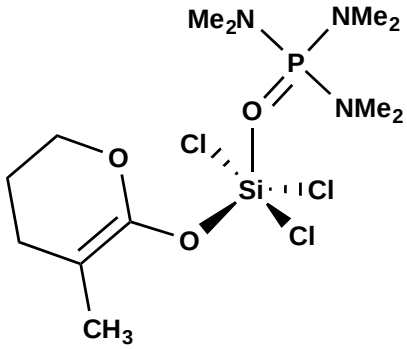
56

| | | | |
|---|---|---|---|
| C | 1.93534233 | -4.67047035 | -1.27010972 |
| C | 2.29934610 | -3.89114546 | -0.02389651 |
| C | 2.34846623 | -3.92373411 | -2.54602080 |
| C | 2.25207757 | -4.61866517 | 1.29203370 |
| O | 2.74459207 | -1.87501402 | -1.27929712 |
| H | 1.82808380 | -4.32114875 | -3.42722687 |
| H | 3.42633754 | -4.03600019 | -2.71665362 |
| C | 2.03221568 | -2.44081155 | -2.38739668 |
| H | 0.95436654 | -2.29168952 | -2.22079066 |
| H | 2.33887304 | -1.85050905 | -3.25547695 |
| C | 2.69944830 | -2.61345649 | -0.12609670 |
| O | 3.05189287 | -1.83340099 | 0.92855802 |
| H | 2.41957840 | -3.94815280 | 2.13874735 |
| H | 0.85333017 | -4.88161284 | -1.28496999 |
| H | 2.42892026 | -5.65329170 | -1.23849094 |
| H | 1.27696020 | -5.10840853 | 1.43429010 |
| P | 6.59397649 | 0.90010821 | 0.50347913 |
| O | 5.42629851 | -0.07165200 | 0.81568652 |

| | | | |
|---|---|---|---|
| C | 7.64184293 | 0.31113416 | -0.85194243 |
| C | 5.82199076 | 2.46918650 | 0.02945667 |
| C | 6.97130757 | 1.21436376 | 3.22276147 |
| C | 9.00584447 | 1.32332759 | 1.88746780 |
| C | 9.74733114 | 1.56842092 | 3.04481314 |
| C | 7.72330416 | 1.45447166 | 4.37238423 |
| C | 9.10718384 | 1.63288231 | 4.28572144 |
| H | 10.82382692 | 1.69993213 | 2.97592670 |
| H | 7.22494649 | 1.49437183 | 5.33653088 |
| H | 9.68847168 | 1.81648307 | 5.18576376 |
| C | 7.68109905 | 0.98949253 | -2.08094411 |
| C | 8.40108089 | -0.85998080 | -0.67468639 |
| C | 9.19435724 | -1.33693258 | -1.71682164 |
| C | 8.48275059 | 0.50737866 | -3.11812133 |
| H | 7.08997756 | 1.88723675 | -2.23315632 |
| H | 8.35586906 | -1.41115595 | 0.25890027 |
| C | 9.23934477 | -0.65265023 | -2.93592692 |
| H | 9.76601665 | -2.25073168 | -1.57996011 |
| H | 9.85966083 | -1.02815330 | -3.74563744 |
| H | 8.50763715 | 1.03545276 | -4.06762987 |
| C | 4.45457338 | 2.49554707 | -0.28250033 |
| C | 6.57995310 | 3.65117139 | -0.01623365 |
| H | 3.86146670 | 1.58910079 | -0.21573936 |
| C | 3.85562429 | 3.70313489 | -0.64959109 |
| C | 4.61046734 | 4.87705249 | -0.70319397 |
| C | 5.97272622 | 4.85174533 | -0.38432079 |
| H | 6.55824938 | 5.76681868 | -0.41027108 |
| H | 7.63523002 | 3.64143401 | 0.24648456 |
| H | 2.79434182 | 3.72270836 | -0.87936886 |
| H | 4.13714155 | 5.81488234 | -0.98159285 |
| C | 7.61528726 | 1.14534362 | 1.97477809 |
| H | 9.51118148 | 1.26032376 | 0.92837155 |
| H | 5.89654329 | 1.06930567 | 3.29777438 |
| Si | 4.52485514 | -1.36879767 | 1.56469444 |
| Cl | 3.42077863 | 0.21822070 | 2.69143799 |
| Cl | 5.29527919 | -2.18385677 | 3.35996129 |
| Cl | 5.71496700 | -2.79780347 | 0.33340702 |
| H | 3.01657934 | -5.40943198 | 1.33479359 |

Table B.29 120 degree enolate complex with HMPA catalyst.





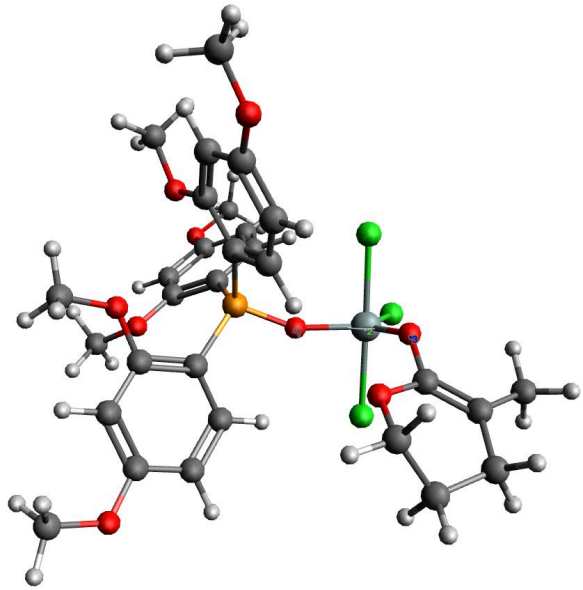

120° O-Si-O enolate free energy: -2875.13079371828

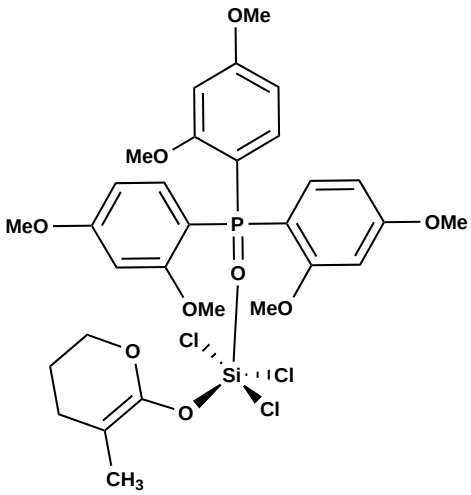
50

| | | | |
|---|---|---|---|
| C | 3.99651531 | -5.81844261 | -1.77695781 |
| C | 4.65748706 | -5.21859424 | -0.55436163 |
| C | 4.29047018 | -5.00958783 | -3.04883983 |
| C | 4.62200105 | -6.02638253 | 0.71436604 |
| O | 5.24015345 | -3.19266261 | -1.73414343 |
| H | 3.56471803 | -5.23704882 | -3.83982507 |
| H | 5.28662540 | -5.25705738 | -3.43741133 |
| C | 4.24900147 | -3.52202880 | -2.72013397 |
| H | 3.26539313 | -3.23254567 | -2.32549288 |
| H | 4.48534125 | -2.89686026 | -3.58632257 |
| C | 5.21405677 | -3.99872055 | -0.61958708 |
| O | 5.92972482 | -3.42990275 | 0.38506716 |
| H | 5.17283293 | -5.54710149 | 1.52626074 |
| H | 2.90818441 | -5.88043444 | -1.61383220 |
| H | 4.33538802 | -6.85700196 | -1.90598770 |
| H | 5.05609162 | -7.02434685 | 0.55543431 |
| P | 6.68610222 | 0.55706167 | 0.32839795 |
| O | 5.80616617 | -0.54630495 | 0.99924417 |
| N | 7.29643045 | 0.11789156 | -1.15217800 |
| N | 5.64714344 | 1.83887729 | 0.19532808 |
| N | 7.94787428 | 1.03999434 | 1.27500744 |
| Si | 5.56250434 | -2.19934169 | 1.46823174 |

| | | | |
|---|---|---|---|
| Cl | 4.92764772 | -2.51096779 | 3.45391452 |
| Cl | 7.72564490 | -2.31769595 | 2.11717403 |
| Cl | 3.45079885 | -1.97548122 | 0.77156601 |
| H | 3.58659854 | -6.18106225 | 1.05334255 |
| C | 9.36332614 | 0.94726779 | 0.91074288 |
| C | 7.69760287 | 1.19553389 | 2.71926366 |
| C | 4.19357577 | 1.68295934 | 0.04174222 |
| C | 6.14453826 | 3.19135074 | -0.06253821 |
| C | 6.53251195 | 0.42377875 | -2.37313839 |
| C | 8.10674781 | -1.11339618 | -1.29425471 |
| H | 6.63237226 | 1.34933579 | 2.90694564 |
| H | 8.24226746 | 2.07671330 | 3.07791975 |
| H | 8.02501771 | 0.30543419 | 3.26769835 |
| H | 9.47582841 | 0.95731825 | -0.17365955 |
| H | 9.81881410 | 0.03558969 | 1.31834035 |
| H | 9.88590063 | 1.81881341 | 1.32252757 |
| H | 8.58485364 | -1.38161215 | -0.35221551 |
| H | 8.87798067 | -0.93470071 | -2.05306700 |
| H | 7.47333600 | -1.95208599 | -1.60268004 |
| H | 7.22195972 | 3.24290184 | 0.10484203 |
| H | 5.65289418 | 3.89598151 | 0.61971111 |
| H | 5.92892273 | 3.50631173 | -1.09434708 |
| H | 6.02462980 | 1.38555185 | -2.28687574 |
| H | 5.79381713 | -0.35863384 | -2.58907836 |
| H | 7.23740840 | 0.48261005 | -3.20989687 |
| H | 3.88501069 | 0.66660340 | 0.28763622 |
| H | 3.88203285 | 1.91418852 | -0.98720180 |
| H | 3.68901201 | 2.37821064 | 0.72338724 |

Table B.30 120 degree enolate complex with 2,4-diOMe-TPPO catalyst.






120° O-Si-O enolate free energy: -3853.50570431028

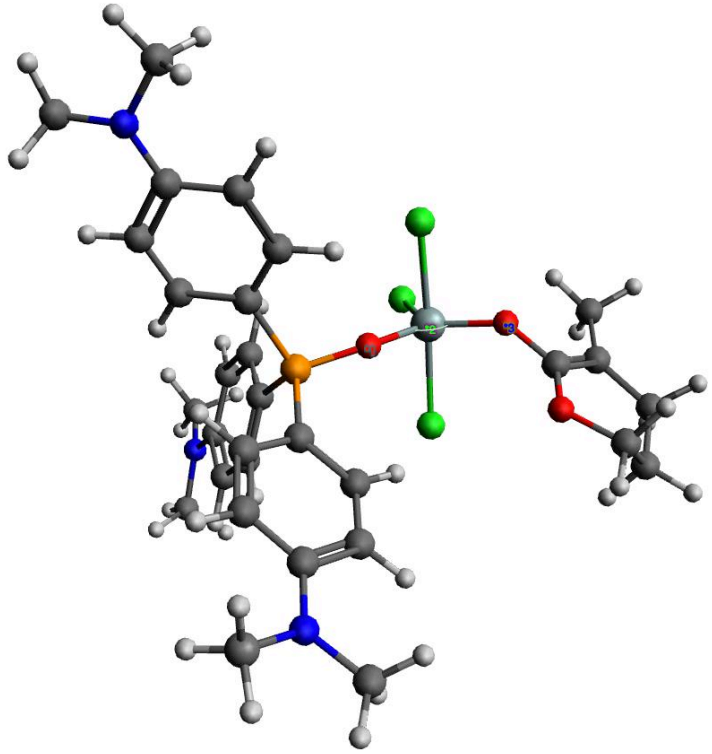
80

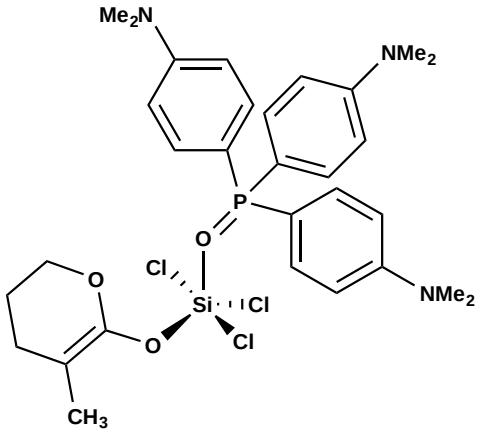
| | | | |
|---|---|---|---|
| C | -0.05290493 | 1.39056373 | 0.00059231 |
| C | 1.03637435 | 0.34090418 | 0.05503689 |
| C | 0.53320132 | 2.80848787 | -0.01901252 |
| C | 0.64779568 | -1.08051062 | -0.24803785 |
| O | 2.73075064 | 1.96809040 | 0.62267689 |
| H | -0.22546065 | 3.56021741 | 0.23457342 |
| H | 0.91429272 | 3.04368107 | -1.02064065 |
| C | 1.68873806 | 2.88939407 | 0.97071851 |
| H | 1.34387636 | 2.65349808 | 1.98918091 |
| H | 2.16626277 | 3.87322276 | 0.97859750 |
| C | 2.30597513 | 0.70085446 | 0.30347880 |
| O | 3.35042547 | -0.16046830 | 0.35630894 |
| H | 1.44220776 | -1.78790500 | 0.00378132 |
| H | -0.74336095 | 1.27165007 | 0.85244381 |
| H | -0.66286191 | 1.23013300 | -0.90128635 |
| H | -0.25136235 | -1.36518704 | 0.31889062 |
| P | 7.20673891 | 1.47568361 | -0.36584593 |
| O | 5.87374482 | 0.73559158 | -0.74615378 |
| C | 8.52300709 | 0.56996291 | -1.21088170 |
| C | 6.93046686 | 3.16301407 | -0.94873313 |
| C | 6.16248569 | 1.81828930 | 2.13005984 |
| C | 8.51994713 | 1.27359818 | 2.17533548 |
| C | 8.49338864 | 1.31930030 | 3.57740285 |
| C | 6.12851085 | 1.88778958 | 3.51242754 |
| C | 7.29845885 | 1.62774066 | 4.23980414 |

| | | | |
|---|---|---|---|
| H | 9.39574635 | 1.12203090 | 4.13881962 |
| H | 5.20840147 | 2.10741132 | 4.04283667 |
| O | 7.18376041 | 1.70140538 | 5.59367880 |
| C | 9.50699943 | 1.13263657 | -2.06183764 |
| C | 8.49904975 | -0.82253346 | -1.05561345 |
| C | 9.40519621 | -1.65865122 | -1.70351090 |
| C | 10.41728212 | 0.30458548 | -2.71937991 |
| O | 9.51085489 | 2.48350341 | -2.20215496 |
| H | 7.74510247 | -1.27595930 | -0.41828462 |
| C | 10.36769833 | -1.08682291 | -2.54304688 |
| H | 9.33019246 | -2.73000377 | -1.56309019 |
| O | 11.29679502 | -1.79319500 | -3.24185472 |
| H | 11.16961131 | 0.70523137 | -3.38738091 |
| C | 5.86061722 | 3.41646007 | -1.82277630 |
| C | 7.71024616 | 4.24815941 | -0.49954380 |
| H | 5.23163775 | 2.59460130 | -2.14923800 |
| C | 5.56883474 | 4.70509692 | -2.24802885 |
| C | 6.34492517 | 5.77590664 | -1.78720063 |
| C | 7.41874624 | 5.55458008 | -0.91051355 |
| H | 8.02089428 | 6.38019685 | -0.55732211 |
| O | 8.74399637 | 3.94384471 | 0.32918443 |
| H | 4.73789858 | 4.89901197 | -2.91783122 |
| O | 5.98570151 | 7.00851338 | -2.23956948 |
| C | 6.70036741 | 8.15341969 | -1.79134429 |
| H | 6.21903499 | 9.00675235 | -2.27201846 |
| H | 7.75437561 | 8.11029767 | -2.09589457 |
| H | 6.63367507 | 8.26309597 | -0.70108195 |
| C | 11.27747179 | -3.21744076 | -3.15716001 |
| H | 12.08138951 | -3.56114082 | -3.80967517 |
| H | 10.32040168 | -3.62124416 | -3.50809067 |
| H | 11.46705478 | -3.55548257 | -2.13102814 |
| C | 8.30942269 | 1.39327647 | 6.40681332 |
| H | 8.63999106 | 0.35853120 | 6.24959289 |
| H | 7.96958914 | 1.51376207 | 7.43671885 |
| H | 9.14217778 | 2.08287958 | 6.21454477 |
| C | 7.34686540 | 1.50912869 | 1.43469214 |
| O | 9.66065626 | 1.02556879 | 1.47635224 |
| H | 5.24149370 | 1.98494462 | 1.57814238 |
| Si | 4.63029677 | -0.45718260 | -0.68699019 |
| Cl | 5.63467482 | -1.48873509 | 1.04129335 |
| Cl | 4.86308364 | -2.21334369 | -1.85873428 |
| Cl | 3.66909036 | 0.57413919 | -2.42641254 |
| H | 0.40928797 | -1.20811861 | -1.31509626 |
| C | 10.81962562 | 0.56888893 | 2.16319756 |
| C | 9.48473224 | 4.98767560 | 0.94774937 |
| C | 10.40129947 | 3.08613089 | -3.13388861 |

| | | | |
|---|---|---|---|
| H | 10.60752281 | -0.34447073 | 2.73302028 |
| H | 11.21894743 | 1.34084995 | 2.83450863 |
| H | 11.55418946 | 0.35210418 | 1.38594803 |
| H | 10.18472004 | 4.15516428 | -3.09430257 |
| H | 10.22135108 | 2.71426410 | -4.15022115 |
| H | 11.44851111 | 2.91320912 | -2.85421934 |
| H | 10.03153631 | 5.58431942 | 0.20573902 |
| H | 10.19710542 | 4.48953849 | 1.60729363 |
| H | 8.83126204 | 5.64105141 | 1.53961240 |

Table B.31 120 degree enolate complex with 4-$NMe_2$-TPPO catalyst.






120° O-Si-O enolate free energy: -3568.27627963716

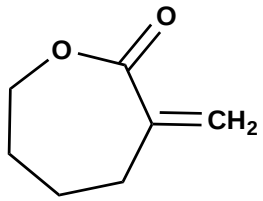
80

| | | | |
|---|---|---|---|
| C | 0.00853513 | 0.43500196 | -2.29543130 |
| C | 0.97073607 | -0.01013533 | -1.21556564 |
| C | 0.36613960 | 1.82838196 | -2.83243384 |
| C | 0.90035711 | -1.44744965 | -0.77611065 |
| O | 1.92885046 | 2.19560022 | -0.99863494 |
| H | -0.47930492 | 2.27933253 | -3.36806792 |
| H | 1.20723567 | 1.75591979 | -3.53372632 |
| C | 0.78048014 | 2.72386867 | -1.67047473 |
| H | -0.03890540 | 2.81740018 | -0.94076162 |
| H | 1.07650419 | 3.72437817 | -1.99803231 |

| | | | |
|---|---|---|---|
| C | 1.85737663 | 0.86109959 | -0.70249902 |
| O | 2.74798482 | 0.54760903 | 0.26989208 |
| H | 1.55663302 | -1.65066202 | 0.07335360 |
| H | -1.02544128 | 0.42595652 | -1.91026181 |
| H | 0.02284241 | -0.29610428 | -3.11841371 |
| H | -0.12651487 | -1.71331157 | -0.48102128 |
| P | 7.04826046 | 1.76594889 | 0.58232426 |
| O | 5.55592333 | 1.27657728 | 0.60916451 |
| C | 8.09989947 | 0.74879618 | -0.45368346 |
| C | 7.00907300 | 3.45237555 | -0.03206606 |
| C | 6.81666002 | 2.01801643 | 3.33496145 |
| C | 9.03696300 | 1.49872021 | 2.54491067 |
| C | 9.51759486 | 1.53769295 | 3.84787015 |
| C | 7.28651135 | 2.06076091 | 4.63863093 |
| C | 8.65459537 | 1.82626562 | 4.93591605 |
| H | 10.56797377 | 1.33336434 | 4.01660306 |
| H | 6.57499744 | 2.25210536 | 5.43263863 |
| N | 9.12509216 | 1.87167789 | 6.23076643 |
| C | 8.62614866 | 1.22742994 | -1.66476558 |
| C | 8.36534702 | -0.58725960 | -0.09682909 |
| C | 9.12538957 | -1.40954929 | -0.91281928 |
| C | 9.39596781 | 0.41573591 | -2.48579332 |
| H | 8.42561939 | 2.24728041 | -1.97829602 |
| H | 7.95762080 | -1.00109391 | 0.82147149 |
| C | 9.66678116 | -0.93147918 | -2.13568329 |
| H | 9.28253149 | -2.43566188 | -0.60342365 |
| N | 10.42831268 | -1.74451104 | -2.94548594 |
| H | 9.76978296 | 0.82953527 | -3.41445463 |
| C | 6.07665044 | 3.82740359 | -1.01534419 |
| C | 7.92327861 | 4.41471595 | 0.42599046 |
| H | 5.34659877 | 3.10520730 | -1.37101371 |
| C | 6.07338038 | 5.11398678 | -1.53694322 |
| C | 7.01225238 | 6.08679182 | -1.10461879 |
| C | 7.92879230 | 5.70357503 | -0.09088485 |
| H | 8.64632149 | 6.41433595 | 0.30207831 |
| H | 8.63745544 | 4.16271765 | 1.20569928 |
| H | 5.32777856 | 5.35931822 | -2.28377014 |
| N | 7.03496885 | 7.35376134 | -1.64486508 |
| C | 7.94564264 | 8.35618358 | -1.11350701 |
| H | 7.83319085 | 9.28077477 | -1.68216677 |
| H | 8.99135136 | 8.03246975 | -1.20215466 |
| H | 7.74362219 | 8.57874525 | -0.05482812 |
| C | 10.52766231 | -3.16873325 | -2.65554425 |
| H | 11.14971312 | -3.64336296 | -3.41575703 |
| H | 9.54422243 | -3.66131525 | -2.65819057 |
| H | 10.99863388 | -3.34497264 | -1.68032746 |

| | | | |
|---|---|---|---|
| C | 10.48423179 | 1.43940063 | 6.52307179 |
| H | 10.65157499 | 0.38660011 | 6.24951658 |
| H | 10.67144561 | 1.54852325 | 7.59239003 |
| H | 11.22066720 | 2.05484404 | 5.99158981 |
| C | 7.68206774 | 1.73747208 | 2.26170326 |
| H | 9.72945205 | 1.26483661 | 1.74107513 |
| H | 5.75710205 | 2.16538638 | 3.15202552 |
| Si | 4.35168195 | 0.07668309 | 0.28124089 |
| Cl | 4.15921783 | -0.21773422 | 2.47677580 |
| Cl | 4.93772226 | -1.94600186 | 0.00276404 |
| Cl | 4.65364351 | 0.48265627 | -1.92429947 |
| H | 1.18379328 | -2.12956141 | -1.59179776 |
| C | 8.19076873 | 2.04430961 | 7.33535174 |
| C | 6.04302436 | 7.74269088 | -2.63646236 |
| C | 10.89664849 | -1.25817768 | -4.23511873 |
| H | 11.54109310 | -2.01394164 | -4.68732384 |
| H | 11.48964287 | -0.34306907 | -4.11795457 |
| H | 10.06949358 | -1.04695085 | -4.93007111 |
| H | 6.25882843 | 8.75575370 | -2.97961968 |
| H | 5.02113521 | 7.72729678 | -2.22964735 |
| H | 6.07428742 | 7.07826505 | -3.50925383 |
| H | 7.64574891 | 2.99182867 | 7.24512462 |
| H | 8.74966686 | 2.06908354 | 8.27204508 |
| H | 7.45626116 | 1.22690917 | 7.39222428 |

Table B.32 Substrate I: alpha-methylene epsilon-caprolactone



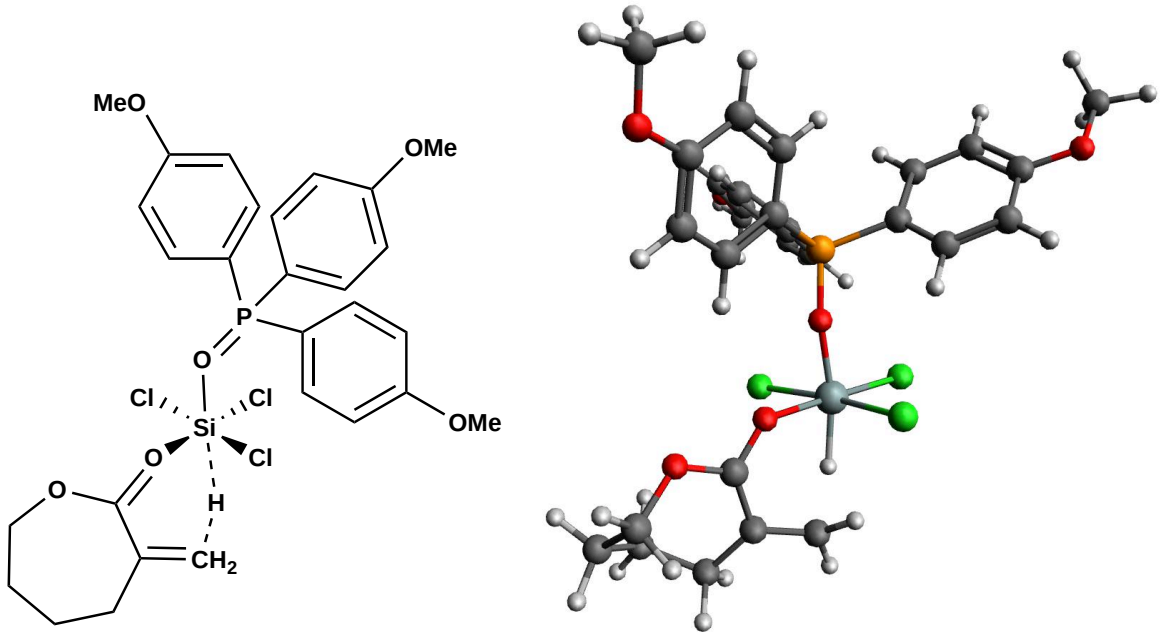

Free Energy: -423.209617292951

19

| | | | |
|---|---|---|---|
| C | 1.00926020 | -0.67025005 | -1.13583266 |
| O | 2.78555102 | 1.04669594 | -1.19520117 |
| C | 1.75370537 | 2.04932263 | -1.09819259 |
| C | 2.46862343 | -0.27505791 | -1.12439367 |
| O | 3.36865043 | -1.08288600 | -1.04879330 |
| C | 0.01159802 | -0.01872677 | -2.09505900 |
| H | -0.48391438 | -0.82625350 | -2.64816746 |
| C | 0.61791488 | 0.97293705 | -3.09976318 |
| H | -0.78015091 | 0.48489249 | -1.52138903 |
| C | 0.65249057 | -1.66063312 | -0.30645924 |
| C | 1.06890387 | 2.28861275 | -2.44102855 |

| | | | |
|---|---|---|---|
| H | 2.27152901 | 2.94516756 | -0.74661149 |
| H | 1.03422131 | 1.75304799 | -0.32603234 |
| H | 1.74369250 | 2.83193170 | -3.11354292 |
| H | 0.20249498 | 2.94116199 | -2.26012072 |
| H | -0.11817843 | 1.19248513 | -3.88212675 |
| H | 1.47046156 | 0.50251049 | -3.60625039 |
| H | -0.37382427 | -2.02022661 | -0.26333007 |
| H | 1.37722086 | -2.13992173 | 0.34430454 |

Table B.33 Transition State of Pathway F with Substrate I




TS Free Energy: -3549.182899

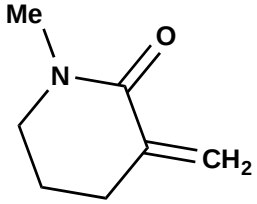
71

C 1.117847 0.063058 -1.148820
O 1.934797 1.989511 -2.409498
C 0.656587 2.105692 -3.075309
C 2.047728 1.130120 -1.382906
O 3.132055 1.272699 -0.740592
P 6.837056 1.663417 0.440032
O 5.363994 1.193594 0.384627
C 7.963416 0.600043 -0.484773
C 6.824833 3.313978 -0.297829
C 6.514329 2.174824 3.151034
C 8.750895 1.520272 2.486015
C 9.194895 1.669280 3.802203
C 6.947026 2.323510 4.459260
C 8.289732 2.073402 4.794074
H 10.231835 1.458975 4.038023

H 6.257455 2.614367 5.245688
O 8.610397 2.244625 6.104069
C 8.728018 1.092497 -1.558935
C 8.054701 -0.760790 -0.151726
C 8.893857 -1.613182 -0.865131
C 9.568701 0.249056 -2.273097
H 8.662926 2.137663 -1.844386
H 7.448162 -1.172942 0.649713
C 9.652516 -1.111362 -1.933450
H 8.926267 -2.662738 -0.595898
O 10.492295 -1.859697 -2.696363
H 10.157959 0.618006 -3.106004
C 5.791661 3.655962 -1.192345
C 7.818926 4.256244 -0.007314
H 4.995055 2.946683 -1.396473
C 5.773595 4.908977 -1.789154
C 6.779524 5.846734 -1.501525
C 7.806822 5.518964 -0.604128
H 8.584947 6.231993 -0.356476
H 8.610488 4.019495 0.698654
H 4.978951 5.188700 -2.474307
O 6.666298 7.045716 -2.134347
C 7.639921 8.053789 -1.881428
H 7.341709 8.909402 -2.489853
H 8.642167 7.721908 -2.182416
H 7.646919 8.342002 -0.822519
C 10.571755 -3.263625 -2.459168
H 11.268949 -3.647087 -3.204909
H 9.593458 -3.742271 -2.589012
H 10.957769 -3.474925 -1.454068
C 9.935548 1.950374 6.533694
H 10.188761 0.899820 6.344387
H 9.945046 2.139805 7.608205
H 10.667373 2.602426 6.041124
C 7.416461 1.773230 2.145282
H 9.456998 1.192535 1.728319
H 5.467258 2.335635 2.911888
Si 4.018740 0.055733 0.491537
Cl 4.770364 -1.056468 -1.343354
Cl 3.085154 1.266959 2.128508
Cl 4.990793 -1.320285 1.907374
C 0.394885 -0.651600 -2.291627
H 0.500209 -1.729523 -2.108812
C 0.913937 -0.336899 -3.704021
H -0.686551 -0.448283 -2.248292
C 1.165629 -0.507941 0.119142

C 0.512015 1.068957 -4.185436
H 0.641545 3.127623 -3.461847
H -0.135039 2.005485 -2.324588
H 1.119026 1.357404 -5.052675
H -0.537939 1.076817 -4.510905
H 0.529506 -1.083205 -4.409727
H 2.005458 -0.435111 -3.713015
H 1.256956 0.103291 1.009900
H 2.739334 -0.842601 0.309282
H 0.693679 -1.479366 0.271739

Table B.34 Substrate H: Lactam

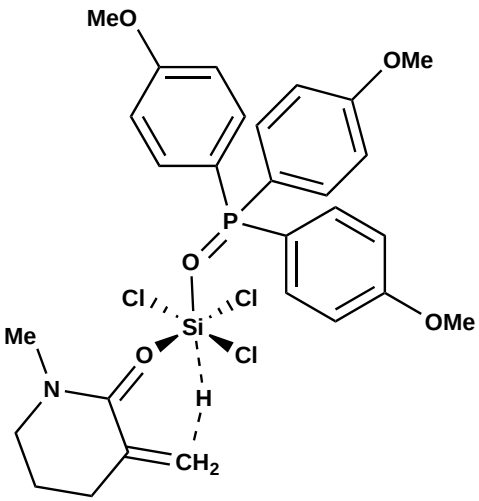


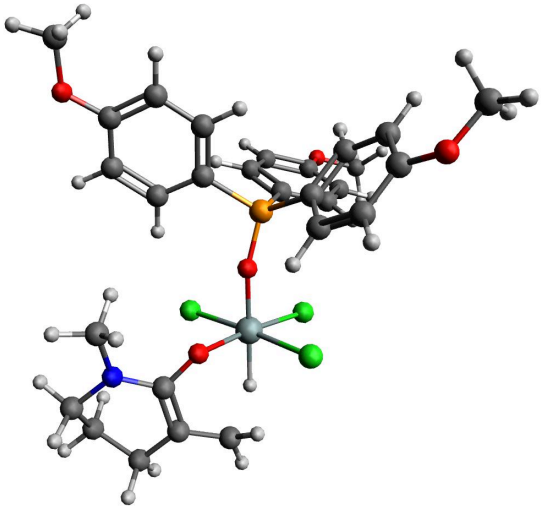

Free Energy: -403.356611518062

20

| | | | |
|---|---|---|---|
| C | -2.03248821 | 0.30031034 | -2.09724457 |
| C | -0.91384644 | -0.01716831 | -1.13188547 |
| C | -1.59914172 | 1.42388416 | -3.04125560 |
| C | -0.59512874 | -1.26074132 | -0.75109532 |
| N | -0.28526099 | 2.36356577 | -1.14494470 |
| H | -2.40361869 | 1.68722162 | -3.73849554 |
| H | -0.73884709 | 1.09560886 | -3.63926018 |
| C | -1.22296764 | 2.65982679 | -2.23077261 |
| H | -2.13056771 | 3.12635296 | -1.81083153 |
| H | -0.75427643 | 3.41069556 | -2.88019437 |
| C | -0.10459624 | 1.12543092 | -0.56806078 |
| O | 0.69030670 | 0.95325558 | 0.35944954 |
| H | 0.21164554 | -1.43332184 | -0.04596943 |
| H | -2.92322464 | 0.62927949 | -1.53844033 |
| H | -2.32189504 | -0.59929293 | -2.65229872 |
| H | -1.13657140 | -2.12309323 | -1.13291836 |
| C | 0.40315905 | 3.51611750 | -0.58095807 |
| H | 1.03437199 | 3.99338592 | -1.34206431 |
| H | 1.02248233 | 3.18451430 | 0.25195346 |
| H | -0.32511463 | 4.25708786 | -0.22197310 |

Table B.35 Transition State of Pathway F with Substrate H



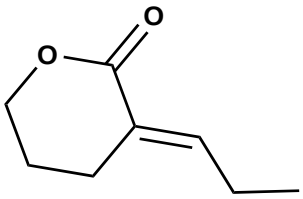
TS Energy: -3529.322559

72

C -0.262642 0.312657 -1.691343
C 0.865330 0.233654 -0.686568
C -0.064146 1.513093 -2.623586
C 1.313074 -0.943092 -0.081801
N 1.299500 2.616741 -0.888587
H -0.934104 1.656137 -3.275652
H 0.813864 1.347368 -3.259122
C 0.160747 2.782009 -1.799641
H -0.747777 3.049253 -1.235340
H 0.394189 3.622241 -2.463029
C 1.645557 1.388578 -0.425590
O 2.775798 1.295566 0.222919
H 1.661890 -0.936523 0.947177
H -1.224678 0.425627 -1.166388
H -0.332924 -0.622432 -2.263810
H 0.892102 -1.894628 -0.413029
P 6.835444 1.597796 0.371277
O 5.352689 1.146506 0.291557
C 8.012806 0.679525 -0.643101
C 6.864993 3.325102 -0.178838
C 6.418936 1.616947 3.115644
C 8.735353 1.416901 2.438918
C 9.136015 1.420753 3.777020
C 6.808458 1.620959 4.446628
C 8.168358 1.522496 4.787071
H 10.190076 1.334587 4.014325
H 6.072804 1.677586 5.242251

O 8.445689 1.528174 6.118221
C 8.468923 1.183606 -1.876723
C 8.455568 -0.586196 -0.228399
C 9.334735 -1.331588 -1.009433
C 9.341907 0.447386 -2.664159
H 8.138412 2.156378 -2.228585
H 8.095397 -1.014297 0.701459
C 9.779008 -0.817755 -2.237500
H 9.639214 -2.312914 -0.664752
O 10.626772 -1.464396 -3.077998
H 9.691088 0.827290 -3.619135
C 6.030972 3.725210 -1.242275
C 7.756083 4.253809 0.371023
H 5.325747 3.017995 -1.672886
C 6.107110 5.017504 -1.745117
C 7.007601 5.942877 -1.189909
C 7.830935 5.559140 -0.121401
H 8.522622 6.258085 0.334524
H 8.394124 3.973794 1.204011
H 5.471631 5.335649 -2.565006
O 7.003489 7.181999 -1.750511
C 7.890702 8.171390 -1.238273
H 7.714937 9.063939 -1.840316
H 8.936757 7.858107 -1.343507
H 7.674441 8.391047 -0.184636
C 11.069382 -2.775973 -2.735485
H 11.710272 -3.092804 -3.559430
H 10.222609 -3.466433 -2.641345
H 11.648075 -2.767423 -1.803104
C 9.797639 1.387943 6.542110
H 10.220286 0.433153 6.205567
H 9.767167 1.408822 7.632517
H 10.417487 2.217127 6.177337
C 7.381530 1.514790 2.091803
H 9.494679 1.327225 1.667182
H 5.363801 1.652411 2.864470
Si 4.061841 -0.026518 -0.128062
Cl 3.905677 -0.590901 2.061992
Cl 5.431179 -1.723034 -0.551137
Cl 4.069124 0.638846 -2.296861
H 2.835506 -1.029630 -0.412115
C 2.007622 3.793971 -0.398493
H 1.496703 4.685381 -0.770409
H 3.049392 3.809235 -0.729315
H 2.005498 3.814866 0.697275

Table B.36 Substrate J: tri-substituted lactone

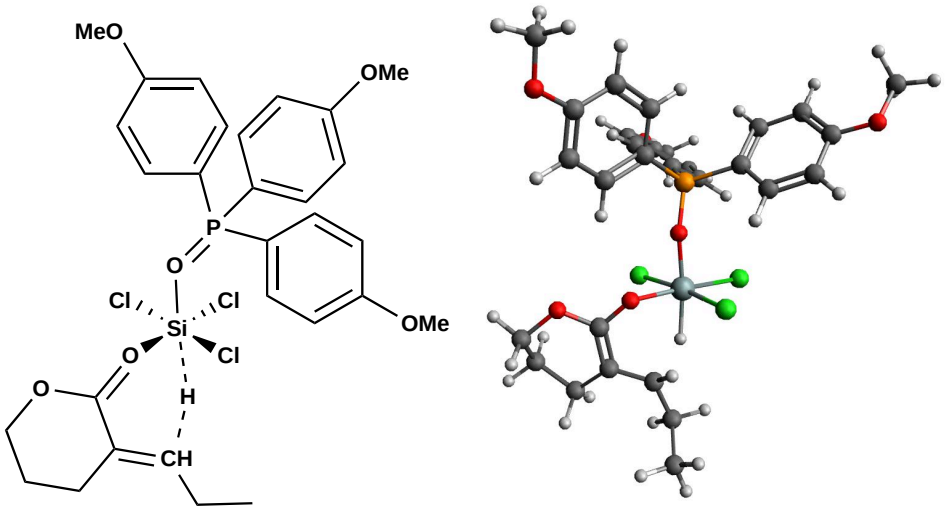


Free Energy: -462.537184713317

22

| | | | |
|---|---|---|---|
| C | -3.72654041 | 3.12762657 | -0.07759678 |
| C | -3.67528073 | 1.63414294 | -0.21915442 |
| C | -2.44347948 | 3.92748111 | 0.05162498 |
| O | -2.46586741 | 1.01517099 | -0.10535836 |
| C | -1.22681886 | 3.10924611 | -0.38747054 |
| C | -1.28379141 | 1.74679324 | 0.28107641 |
| H | -2.30653697 | 4.23951846 | 1.09942424 |
| H | -2.51899320 | 4.85308267 | -0.53256946 |
| H | -0.29378924 | 3.61679949 | -0.11363750 |
| H | -1.22193669 | 2.97655166 | -1.47732097 |
| H | -0.45242900 | 1.10029007 | -0.01048959 |
| H | -1.27781824 | 1.84514413 | 1.37563463 |
| O | -4.64686543 | 0.94223622 | -0.44681998 |
| C | -4.94674794 | 3.69776450 | -0.07001886 |
| C | -5.21940367 | 5.17361018 | 0.06327997 |
| H | -5.80464373 | 3.03426793 | -0.16915037 |
| C | -6.71409754 | 5.50959545 | 0.13649831 |
| H | -4.76467271 | 5.70581652 | -0.78770521 |
| H | -4.70676181 | 5.56593829 | 0.95460613 |
| H | -7.24038628 | 5.16078796 | -0.76006973 |
| H | -6.87063526 | 6.59091673 | 0.21925292 |
| H | -7.18383402 | 5.03392880 | 1.00581419 |

Table B.37 Transition State of Pathway F with Substrate J




TS Energy: -3588.515008

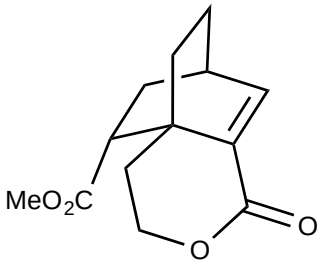
74

C -5.310024 -1.162093 -2.424561
C -4.554734 -0.787288 -1.162562
C -4.743191 -0.423182 -3.645359
C -4.626083 -1.489386 0.057394
O -3.418497 1.068081 -2.225467
H -5.468907 -0.423670 -4.468633
H -3.836732 -0.922830 -4.005282
C -4.412264 1.015996 -3.274203
H -5.305347 1.556726 -2.931911
H -3.961171 1.567924 -4.102372
C -3.575940 0.224326 -1.191179
O -2.702593 0.361216 -0.262403
H -4.495061 -0.902556 0.965923
H -6.374762 -0.909251 -2.305546
H -5.269275 -2.244358 -2.598203
C -5.451052 -2.739313 0.249726
P 1.152226 0.310166 0.532889
O -0.359700 -0.024522 0.561896
C 2.103605 -0.646051 -0.665807
C 1.216335 2.058593 0.073095
C 1.065733 0.213142 3.306952
C 3.248084 -0.182635 2.327439
C 3.810241 -0.291968 3.601427
C 1.616571 0.101254 4.573733
C 2.990825 -0.148494 4.730670
H 4.869939 -0.499355 3.697347
H 0.996241 0.187902 5.460522

O 3.429901 -0.241951 6.014263
C 2.577160 -0.059723 -1.855025
C 2.323489 -2.015577 -0.450244
C 2.999365 -2.787325 -1.392509
C 3.256157 -0.819909 -2.795775
H 2.407145 0.994606 -2.048756
H 1.941408 -2.497225 0.444774
C 3.466105 -2.190538 -2.573861
H 3.134765 -3.846164 -1.204720
O 4.127766 -2.852335 -3.559203
H 3.621470 -0.377653 -3.717600
C 0.145604 2.616573 -0.652695
C 2.308163 2.866409 0.410432
H -0.725452 2.011161 -0.887191
C 0.187550 3.948009 -1.042981
C 1.292330 4.750798 -0.712906
C 2.356410 4.207322 0.022203
H 3.211488 4.810116 0.305824
H 3.133874 2.461881 0.990371
H -0.634167 4.392259 -1.596562
O 1.234747 6.040423 -1.141434
C 2.307103 6.921609 -0.823237
H 2.034338 7.884902 -1.256818
H 3.250225 6.575243 -1.265128
H 2.423699 7.028644 0.262725
C 4.328763 -4.257799 -3.430790
H 4.854280 -4.562245 -4.337274
H 3.371719 -4.789699 -3.364023
H 4.945754 -4.491372 -2.554021
C 4.807230 -0.511900 6.255507
H 5.102534 -1.479162 5.829678
H 4.914645 -0.543585 7.340768
H 5.445339 0.282487 5.847432
C 1.880376 0.073897 2.165410
H 3.889128 -0.313116 1.459763
H -0.002969 0.375234 3.196762
Si -1.747566 -1.113620 0.494394
Cl -2.466987 -0.380823 2.496758
Cl -0.726166 -2.856586 1.395840
Cl -1.238061 -1.778902 -1.602791
H -3.119470 -1.917854 0.356571
H -5.581428 -3.277468 -0.695111
C -6.825497 -2.413673 0.871354
H -4.908570 -3.410995 0.925640
H -7.386821 -1.695532 0.261288
H -6.706196 -1.984406 1.873167

H -7.428848 -3.324897 0.962256

Table B.38 Substrate K: tricyclic lactone



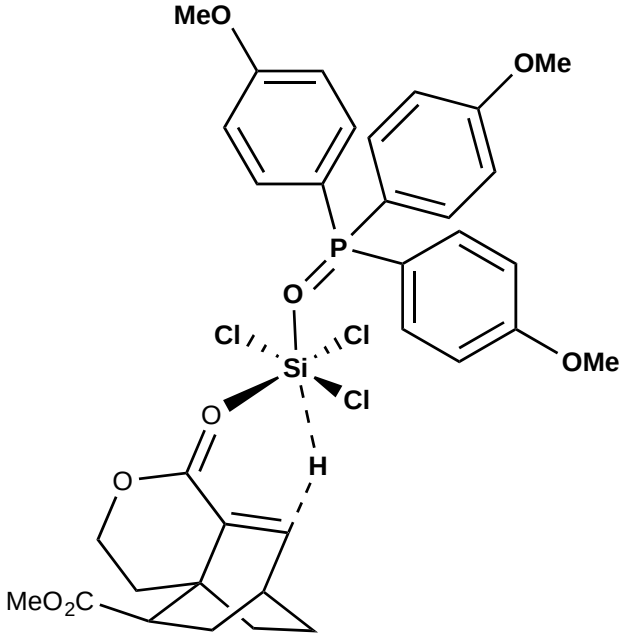

Free Energy: -805.917624865108

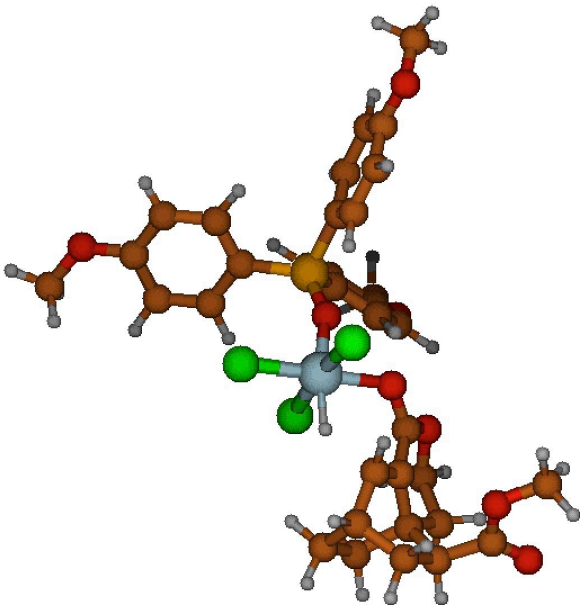
33

| | | | |
|---|---|---|---|
| C | -2.80195204 | -1.26077934 | 2.66506773 |
| C | -1.32354999 | -0.77473034 | 2.65664854 |
| H | -2.88047864 | -2.33997768 | 2.81234987 |
| C | -3.49855239 | -0.84636295 | 1.33594713 |
| H | -3.33167712 | -0.79792599 | 3.50631573 |
| C | -0.96961318 | -0.17921123 | 1.22711272 |
| C | -0.28190651 | -1.71612697 | 3.28292507 |
| H | -1.24183490 | 0.08361025 | 3.32931150 |
| C | -1.88079243 | 1.08582612 | 1.09981483 |
| C | -3.37816258 | 0.70045195 | 1.21523646 |
| H | -1.67795236 | 1.55291839 | 0.12997354 |
| H | -1.59397363 | 1.81145527 | 1.87139975 |
| C | -1.43018216 | -1.13791693 | 0.14607401 |
| C | 0.51053043 | 0.19558115 | 1.04951089 |
| C | -2.73682751 | -1.46129812 | 0.19469598 |
| H | -4.54853860 | -1.15455826 | 1.34598435 |
| H | -3.84170524 | 1.16166609 | 2.09610502 |
| H | -3.93745700 | 1.04870440 | 0.34081947 |
| O | 0.80118294 | -1.44147892 | -0.77143067 |
| H | 0.95148978 | 0.52230654 | 1.99830026 |
| H | 0.58680069 | 1.03553219 | 0.34691046 |
| C | 1.32427785 | -0.96365194 | 0.49162616 |
| H | 1.37820792 | -1.80773136 | 1.18865750 |
| H | 2.34795071 | -0.65888607 | 0.26447121 |
| C | -0.53344705 | -1.65425789 | -0.92244174 |
| O | -0.93040998 | -2.23313814 | -1.91370485 |
| H | -3.19695665 | -2.12081812 | -0.53669562 |
| O | 0.55476723 | -1.25419395 | 4.03254727 |
| O | -0.28514409 | -3.06801261 | 3.12804325 |
| C | -0.75765379 | -3.81660870 | 1.99733955 |
| H | -0.69147404 | -4.85988281 | 2.31047288 |
| H | -0.10299926 | -3.66040961 | 1.13521164 |

H -1.78453641 -3.58081443 1.72057010

Table B.39 Transition State of Pathway F with Substrate K



TS Energy: -3931.916448

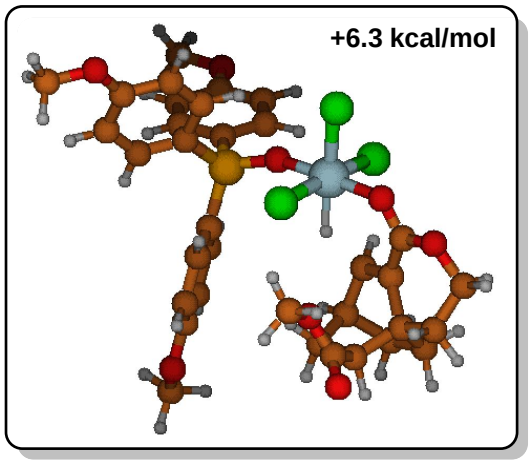
85

C 0.258368 -0.872540 -0.370754
C 1.359023 -0.226184 -1.184141
C 0.011696 -0.057497 0.911878
C 1.632147 -0.820799 -2.409044
O 2.067497 1.273842 0.552404
H -0.497253 -0.672874 1.665124
H -0.640853 0.797219 0.711862
C 1.323414 0.453954 1.495465
H 1.991688 -0.360199 1.793922
H 1.152271 1.106172 2.353039
C 2.231382 0.759547 -0.680500
O 3.253999 1.147195 -1.326218
H 3.386493 -1.047563 -2.270269
C 0.669482 -2.346292 -0.077366
C -1.017931 -0.977642 -1.306378
C 0.883627 -2.112052 -2.596085
P 7.055932 1.531357 -0.707500
O 5.777171 1.051951 -1.444219
C 8.393752 0.325168 -0.686423
C 7.588247 3.012809 -1.595420
C 5.321353 2.373452 1.287670
C 7.590335 1.938210 2.016825

C 7.257594 2.326874 3.317050
C 4.984699 2.761164 2.575245
C 5.948184 2.741959 3.597815
H 8.014147 2.286160 4.091962
H 3.971412 3.065673 2.816654
O 5.512606 3.132243 4.826546
C 9.578928 0.522442 -1.419558
C 8.228003 -0.866019 0.037049
C 9.227369 -1.836180 0.049175
C 10.579847 -0.440620 -1.412910
H 9.718183 1.427844 -2.002018
H 7.299130 -1.057324 0.567382
C 10.410219 -1.625647 -0.677398
H 9.062439 -2.752446 0.604057
O 11.442450 -2.507442 -0.731094
H 11.496736 -0.302113 -1.977534
C 7.175943 3.206015 -2.928290
C 8.408295 3.970929 -0.988292
H 6.516030 2.486685 -3.404393
C 7.589960 4.329497 -3.630549
C 8.418281 5.283281 -3.019145
C 8.829115 5.103019 -1.688869
H 9.458730 5.832034 -1.191222
H 8.722299 3.852830 0.045746
H 7.271829 4.493044 -4.655303
O 8.759891 6.349608 -3.790844
C 9.583513 7.369813 -3.235484
H 9.708207 8.109659 -4.027211
H 10.565871 6.973939 -2.946027
H 9.103157 7.840272 -2.368077
C 11.316493 -3.755224 -0.053656
H 12.247407 -4.289277 -0.248460
H 10.471022 -4.333383 -0.445594
H 11.196781 -3.608431 1.026958
C 6.423892 3.111958 5.920405
H 6.805719 2.099065 6.099944
H 5.849886 3.443356 6.787240
H 7.262674 3.799709 5.752487
C 6.636261 1.961826 0.993404
H 8.601197 1.596562 1.816006
H 4.558676 2.355368 0.515954
Si 4.609512 -0.141458 -1.992852
H 1.946792 -0.231914 -3.267071
Cl 6.060553 -1.623956 -2.680105
Cl 4.412451 0.805784 -3.988836
Cl 4.528075 -1.139581 0.140490

H -1.781450 -1.518302 -0.736626
C -0.636292 -1.770537 -2.594992
C -1.647199 0.381234 -1.583381
H -0.894352 -1.201151 -3.490105
H -1.196863 -2.711657 -2.635569
C 1.172662 -3.026844 -1.377861
H 1.162377 -2.611368 -3.527663
H 2.250075 -3.206716 -1.315546
H 0.686827 -3.997601 -1.529382
H -0.197936 -2.873453 0.342615
H 1.457643 -2.360627 0.681600
O -2.516997 0.878071 -0.889996
O -1.129159 1.001466 -2.662303
C -1.638551 2.317009 -2.950787
H -1.463116 2.984643 -2.104582
H -2.710461 2.270461 -3.159471
H -1.085464 2.652743 -3.827631

Table B.40 Transition State with Substrate K (+6.3 kcal/mol).



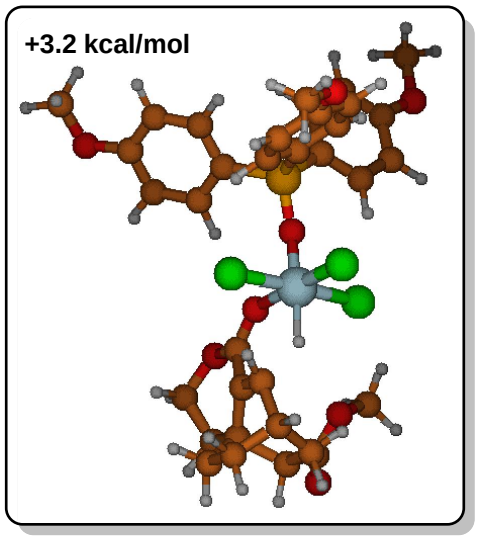

TS-Kc
TS Free Energy: -3931.903374
85

C 0.337138 -1.535976 -1.081228
C 0.929515 -0.350223 -0.327552
C -1.074216 -1.181351 -1.593382
C 2.186911 -0.574772 0.265130
O -0.921512 1.101356 -0.703016
H -1.717024 -2.071812 -1.613792
H -1.036712 -0.799939 -2.618794
C -1.715964 -0.109726 -0.717391
H -1.835091 -0.445441 0.319889
H -2.687106 0.204353 -1.102028
C 0.355948 0.924693 -0.327435

Cl 2.433479 4.423235 0.474969
H 2.385205 -0.237946 1.278771
C 0.327908 -2.720316 -0.062525
C 1.312277 -2.040131 -2.220566
C 2.755273 -1.915850 -0.123876
P 6.092782 2.311722 0.008119
Cl 3.100383 2.599010 -2.074478
C 6.431574 0.731498 -0.811113
C 6.636370 3.644229 -1.081026
C 6.366255 2.229701 2.780863
C 8.430031 2.540842 1.553799
C 9.149535 2.569949 2.749464
C 7.075434 2.258071 3.974975
C 8.469432 2.425400 3.968553
H 10.223099 2.718657 2.718580
H 6.563262 2.164180 4.928067
O 9.070022 2.440990 5.188987
C 6.087818 0.545321 -2.168353
C 7.002446 -0.338459 -0.109783
C 7.240022 -1.567126 -0.733407
C 6.324947 -0.667348 -2.795937
H 5.615852 1.349396 -2.723839
H 7.273194 -0.224657 0.936050
C 6.902380 -1.733514 -2.083331
H 7.687309 -2.372024 -0.163028
O 7.092174 -2.878921 -2.788438
H 6.061109 -0.818148 -3.838392
C 5.935546 4.866292 -1.047106
C 7.751559 3.519426 -1.919264
H 5.044438 4.965158 -0.434572
C 6.356389 5.933266 -1.825195
C 7.482919 5.805569 -2.655551
C 8.182036 4.591507 -2.705611
H 9.042108 4.464635 -3.352562
H 8.290979 2.578542 -1.983442
H 5.814372 6.874078 -1.820948
O 7.809400 6.909408 -3.379910
C 8.906667 6.841675 -4.284171
H 8.955556 7.822217 -4.761354
H 8.743515 6.070459 -5.046933
H 9.848177 6.645410 -3.753986
C 7.680676 -4.003529 -2.137403
H 7.724070 -4.789393 -2.892047
H 7.066044 -4.339829 -1.292944
H 8.695938 -3.772831 -1.788287
C 10.479476 2.624650 5.261411

H 11.012263 1.814827 4.746458
H 10.724257 2.603102 6.325056
H 10.776218 3.591897 4.837041
C 7.040486 2.361306 1.552064
H 8.972605 2.671672 0.620097
H 5.285368 2.120627 2.796918
Si 2.808091 2.330653 0.145878
H 2.991258 0.720915 -0.132765
O 0.986246 2.014616 -0.089372
O 4.618819 2.524044 0.413318
Cl 2.626694 1.847449 2.339154
H 0.983105 -3.053876 -2.474179
C 2.764401 -2.084983 -1.656234
C 1.176508 -1.298311 -3.540995
H 3.372984 -1.296147 -2.102932
H 3.227916 -3.045412 -1.914076
C 1.763105 -2.954168 0.495024
H 3.759008 -2.062007 0.287735
H 1.777811 -2.869305 1.586489
H 2.118931 -3.961784 0.246934
H -0.044111 -3.623268 -0.563619
H -0.372611 -2.492654 0.750292
O 0.552458 -1.739458 -4.491698
O 1.788216 -0.106576 -3.547774
C 1.659779 0.674954 -4.752241
H 0.604746 0.866627 -4.965948
H 2.106420 0.139497 -5.594292
H 2.188365 1.604846 -4.543642

Table B.41 Transition State with Substrate K (+3.2 kcal/mol).



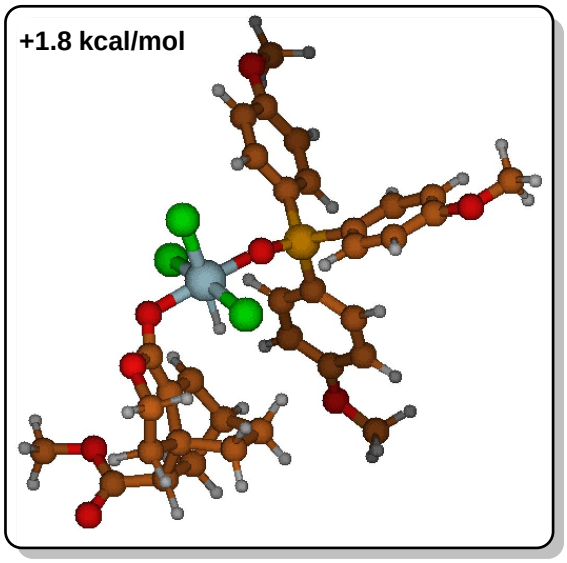

TS-Kb Free Energy: -3931.908380

85

C -0.243512 -0.735637 -0.454821
C 1.279833 -0.645741 -0.374168
C -0.900372 0.454840 0.278162
C 1.965166 -1.749581 -0.922234
O 1.288983 1.509166 0.639017
H -1.798259 0.124414 0.816240
H -1.228710 1.227414 -0.423344
C 0.064153 1.080416 1.279412
H 0.332899 0.376144 2.077214
H -0.343916 1.987562 1.729351
C 1.948871 0.526400 -0.008091
O 3.151230 0.836747 -0.328389
H 2.832656 -2.178856 -0.433092
C -0.633065 -2.101517 0.193102
C -0.713639 -0.880001 -1.959763
C 1.041442 -2.706435 -1.628472
P 6.948298 1.591523 -0.529692
O 5.539483 1.157667 -1.017770
C 8.269849 0.403594 -0.829035
C 7.323591 3.111739 -1.434834
C 5.604169 2.283605 1.794950
C 7.987254 1.935237 2.060433
C 7.895151 2.268726 3.414054
C 5.505791 2.615107 3.137989
C 6.648774 2.611891 3.955778
H 8.787884 2.244218 4.028910
H 4.547506 2.867011 3.581673
O 6.443198 2.946245 5.258034
C 9.200147 0.610747 -1.867543
C 8.345377 -0.779951 -0.077929
C 9.321392 -1.736685 -0.347919
C 10.175431 -0.335995 -2.142098
H 9.156152 1.511488 -2.471283
H 7.616153 -0.978506 0.699888
C 10.239430 -1.518892 -1.387112
H 9.343421 -2.647587 0.238791
O 11.221271 -2.388616 -1.738224
H 10.890937 -0.188540 -2.944841
C 6.677720 3.361843 -2.660644
C 8.257157 4.036956 -0.951956
H 5.927885 2.668687 -3.032155
C 6.976500 4.508326 -3.385186
C 7.920756 5.427760 -2.900702
C 8.563021 5.190717 -1.675754

H 9.285574 5.892082 -1.274140
H 8.752317 3.874224 0.001554
H 6.479740 4.714656 -4.328419
O 8.139783 6.520096 -3.681235
C 9.087604 7.493013 -3.254142
H 9.103974 8.251676 -4.037983
H 10.087419 7.053754 -3.148445
H 8.782821 7.952690 -2.305659
C 11.302388 -3.644932 -1.069036
H 12.125968 -4.178206 -1.546090
H 10.374169 -4.216962 -1.189462
H 11.520774 -3.512048 -0.001987
C 7.552098 2.950455 6.151379
H 7.997724 1.951168 6.234411
H 7.148582 3.250949 7.119351
H 8.315733 3.671521 5.832935
C 6.853458 1.942689 1.238470
H 8.956158 1.650448 1.658390
H 4.709388 2.260231 1.179832
Si 4.356825 -0.088941 -1.446120
H 3.066001 -0.998493 -1.793415
Cl 5.691115 -1.322018 -2.676966
Cl 3.739354 1.165433 -3.207484
Cl 4.858814 -1.311420 0.410985
H -1.760761 -1.198903 -1.923035
C 0.152130 -1.977092 -2.654702
C -0.783891 0.440721 -2.710631
H 0.777085 -1.537788 -3.435937
H -0.506859 -2.711714 -3.132897
C 0.128526 -3.269217 -0.493632
H 1.599774 -3.517051 -2.106157
H 0.736419 -3.821779 0.230832
H -0.570744 -3.987025 -0.939632
H -1.718936 -2.237678 0.102696
H -0.404056 -2.065122 1.264174
O -1.821176 1.069822 -2.849025
O 0.399058 0.856179 -3.175867
C 0.406604 2.117853 -3.876540
H 0.000927 2.905095 -3.236221
H -0.198470 2.040853 -4.784079
H 1.453300 2.301327 -4.108064

Table B.42 Transition State with Substrate K (+1.8 kcal/mol).




TS-Ka Free Energy: -3931.910566

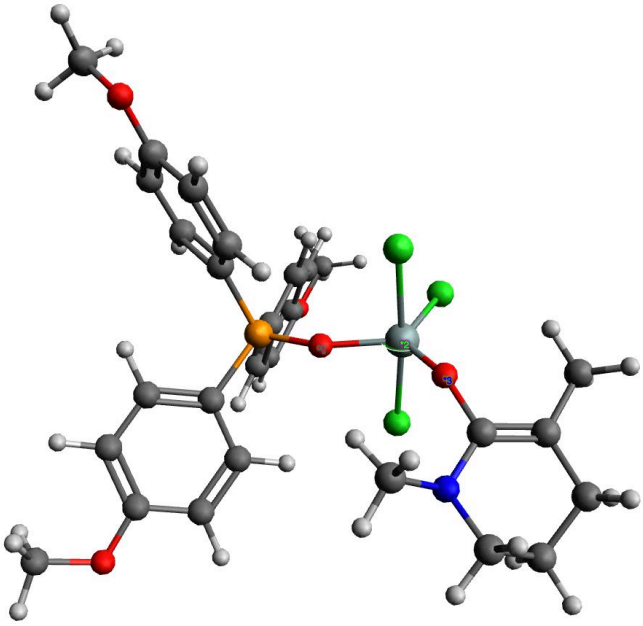
85

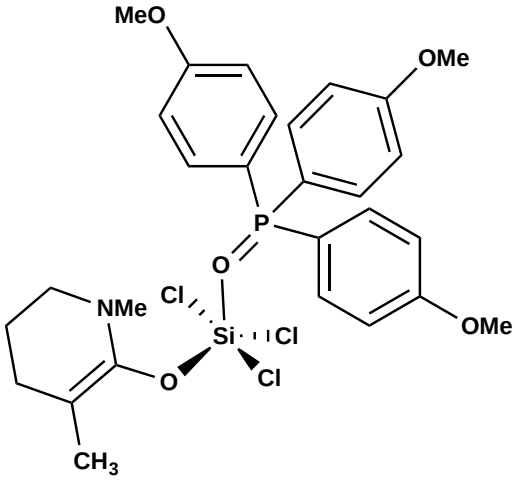
C 0.393819 -1.215418 -0.772333
C 1.066707 0.039438 -1.282281
C -1.019124 -0.866055 -0.270634
C 2.318702 -0.137089 -1.858691
O -0.530894 1.560578 -0.341015
H -1.401585 -1.653197 0.392893
H -1.719012 -0.796044 -1.109664
C -1.028510 0.463672 0.474048
H -0.407686 0.439821 1.375454
H -2.041750 0.763072 0.748187
C 0.618204 1.342789 -0.991924
Cl 2.757163 4.607574 -0.156252
H 3.281605 1.047568 -1.012888
C 1.303546 -1.835396 0.328263
C 0.390433 -2.283763 -1.947027
C 2.825358 -1.544526 -1.694331
P 6.338171 2.315797 -0.104565
Cl 3.793821 2.981199 -2.770170
C 6.676224 0.686768 -0.824476
C 7.216365 3.553034 -1.083975
C 6.012797 2.235506 2.654333
C 8.303524 2.474042 1.899667
C 8.747917 2.501816 3.222555
C 6.448328 2.261945 3.972472
C 7.815247 2.395707 4.265995
H 9.806356 2.619794 3.424254

H 5.740637 2.193590 4.793004
O 8.137396 2.420823 5.587256
C 6.516693 0.482505 -2.212435
C 7.092266 -0.388042 -0.028458
C 7.352826 -1.642220 -0.586877
C 6.771722 -0.758529 -2.774757
H 6.172252 1.294483 -2.847088
H 7.217983 -0.257214 1.042282
C 7.193457 -1.830095 -1.967016
H 7.672606 -2.452625 0.058142
O 7.418574 -3.002419 -2.616137
H 6.648235 -0.925132 -3.840834
C 6.649614 4.837536 -1.208100
C 8.447600 3.287967 -1.695337
H 5.675349 5.045660 -0.775457
C 7.313749 5.827783 -1.915547
C 8.553076 5.557438 -2.521082
C 9.121994 4.279978 -2.410996
H 10.069161 4.042021 -2.882724
H 8.890017 2.297050 -1.635632
H 6.879782 6.816240 -2.031886
O 9.116352 6.592477 -3.199507
C 10.353019 6.384902 -3.873568
H 10.594941 7.338717 -4.344486
H 10.258452 5.609294 -4.644358
H 11.149199 6.112195 -3.169053
C 7.817141 -4.144465 -1.862042
H 7.910287 -4.955541 -2.585496
H 7.061143 -4.407471 -1.111303
H 8.784682 -3.978361 -1.371875
C 9.500375 2.592383 5.962299
H 10.123285 1.769975 5.587547
H 9.507884 2.586146 7.053346
H 9.894047 3.550306 5.599026
C 6.942096 2.335300 1.600773
H 9.035461 2.576593 1.102958
H 4.951394 2.148551 2.434739
Si 3.125534 2.560210 -0.656311
H 2.646691 0.465287 -2.703623
O 1.322455 2.369197 -1.266114
O 4.841793 2.681094 -0.030048
Cl 2.497077 1.756296 1.427588
H 0.028302 -3.221275 -1.511615
C 1.845584 -2.463084 -2.481850
C -0.622539 -1.960348 -3.035788
H 1.895442 -2.233736 -3.549488

H 2.167035 -3.504455 -2.356332
C 2.763524 -1.937897 -0.197603
H 3.842761 -1.656322 -2.078958
H 3.419027 -1.273444 0.373906
H 3.150641 -2.957953 -0.080742
H 0.908397 -2.823303 0.600384
H 1.272289 -1.208244 1.223940
O -1.744265 -2.431374 -3.079252
O -0.163087 -1.075714 -3.944100
C -1.087230 -0.676010 -4.975225
H -1.971079 -0.209752 -4.532506
H -1.392882 -1.542884 -5.567192
H -0.540181 0.040706 -5.588118

Table B.43 120 degree enolate complex with substrate H.






Free Energy: -3529.37516685634

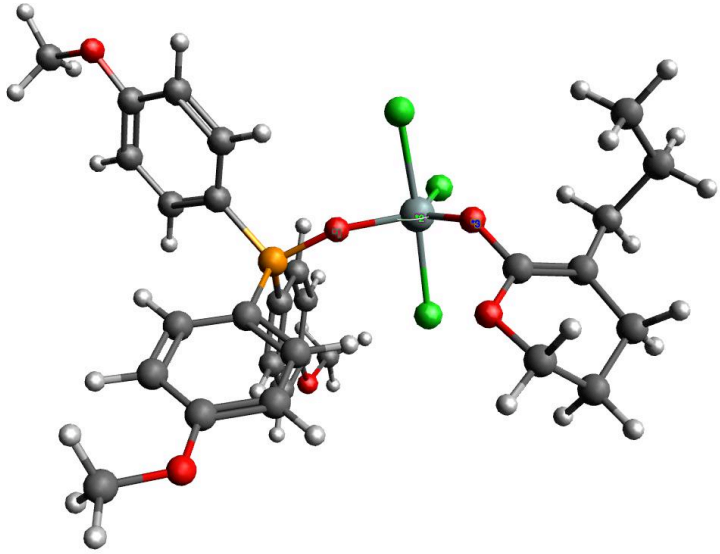
72

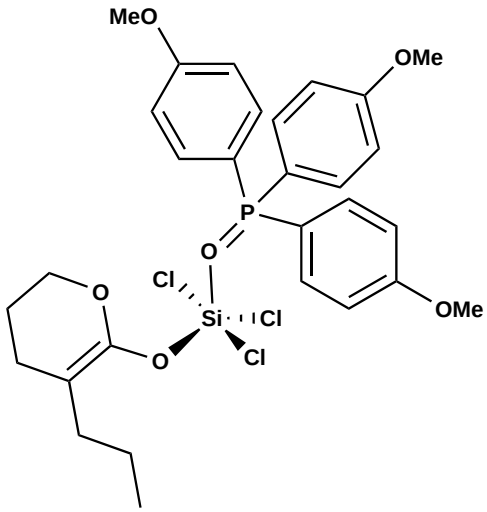
| | | | |
|---|---|---|---|
| C | -0.19797949 | 0.24845344 | -2.18854943 |
| C | 0.89669882 | -0.08409492 | -1.19827071 |
| C | 0.00152222 | 1.64198991 | -2.79352559 |
| C | 1.04640765 | -1.53338704 | -0.82082913 |
| N | 1.60828794 | 2.25960916 | -1.03522528 |
| H | -0.90111051 | 1.97962499 | -3.31875573 |
| H | 0.82127385 | 1.61382379 | -3.52323467 |
| C | 0.35936140 | 2.63793206 | -1.69415323 |
| H | -0.46663519 | 2.68892622 | -0.95551194 |
| H | 0.48990297 | 3.64613593 | -2.10648157 |

| | | | |
|---|---|---|---|
| C | 1.71108298 | 0.88716372 | -0.73052006 |
| O | 2.71332073 | 0.60248309 | 0.16614066 |
| H | 1.74005340 | -1.68323764 | 0.00985671 |
| H | -1.18946072 | 0.17455375 | -1.70987935 |
| H | -0.20120828 | -0.50629493 | -2.99025800 |
| H | 0.07214404 | -1.94755854 | -0.51906285 |
| P | 6.96656792 | 1.82721801 | 0.45891030 |
| O | 5.46504798 | 1.38437248 | 0.41633107 |
| C | 8.02530495 | 0.77546768 | -0.54605937 |
| C | 7.01530668 | 3.52724767 | -0.14135922 |
| C | 6.62545287 | 2.00566091 | 3.21092856 |
| C | 8.89694903 | 1.58563558 | 2.48045563 |
| C | 9.33654102 | 1.60867589 | 3.80584250 |
| C | 7.05327336 | 2.02989073 | 4.52862853 |
| C | 8.41049721 | 1.82991663 | 4.83666366 |
| H | 10.38661866 | 1.44241626 | 4.01745806 |
| H | 6.34904690 | 2.17630844 | 5.34162864 |
| O | 8.72523227 | 1.85995092 | 6.15661291 |
| C | 8.54512618 | 1.21173114 | -1.78087428 |
| C | 8.28687549 | -0.53871533 | -0.12575370 |
| C | 9.05229423 | -1.40099529 | -0.90706225 |
| C | 9.31231995 | 0.36133720 | -2.56229506 |
| H | 8.34367037 | 2.21715664 | -2.13709790 |
| H | 7.87882505 | -0.90976380 | 0.81027551 |
| C | 9.57063041 | -0.95189609 | -2.13192329 |
| H | 9.22160179 | -2.41428073 | -0.56183594 |
| O | 10.32934662 | -1.70730688 | -2.96462290 |
| H | 9.71467787 | 0.68774365 | -3.51638985 |
| C | 6.20299400 | 3.90708782 | -1.23074068 |
| C | 7.85923356 | 4.47889018 | 0.44620676 |
| H | 5.52973494 | 3.18457188 | -1.68557841 |
| C | 6.25431351 | 5.20418692 | -1.71959715 |
| C | 7.10953169 | 6.15206568 | -1.12969745 |
| C | 7.91230701 | 5.78646002 | -0.03931589 |
| H | 8.56600187 | 6.50397650 | 0.44247492 |
| H | 8.47531008 | 4.21352888 | 1.30052411 |
| H | 5.63395665 | 5.50976785 | -2.55656469 |
| O | 7.08449226 | 7.39340018 | -1.67850708 |
| C | 7.92721963 | 8.40606777 | -1.13330228 |
| H | 7.75019818 | 9.29476255 | -1.74061289 |
| H | 8.98462407 | 8.12034387 | -1.20089611 |
| H | 7.66627359 | 8.61829088 | -0.08870067 |
| C | 10.59796129 | -3.06411587 | -2.61196583 |
| H | 11.21262484 | -3.46230825 | -3.42023676 |
| H | 9.66940733 | -3.64275795 | -2.53699130 |
| H | 11.15172011 | -3.12310997 | -1.66672035 |

| | | | |
|---|---|---|---|
| C | 10.07309113 | 1.61820658 | 6.55148265 |
| H | 10.40215521 | 0.61851232 | 6.24120580 |
| H | 10.07569599 | 1.68186457 | 7.64042785 |
| H | 10.74960553 | 2.37660163 | 6.13778960 |
| C | 7.54543492 | 1.78144727 | 2.16641183 |
| H | 9.62169534 | 1.40073572 | 1.69262331 |
| H | 5.57034126 | 2.12174178 | 2.99001435 |
| Si | 4.30143018 | 0.12359117 | 0.04050193 |
| Cl | 4.26785220 | -0.36444889 | 2.21208930 |
| Cl | 4.93384092 | -1.85290165 | -0.42470059 |
| Cl | 4.51708942 | 0.70147803 | -2.12454585 |
| H | 1.39895174 | -2.14068710 | -1.66900131 |
| C | 2.00055284 | 3.20344413 | 0.00533295 |
| H | 1.97689610 | 4.21139014 | -0.42289850 |
| H | 3.01454849 | 3.00078549 | 0.34983564 |
| H | 1.32375053 | 3.17935613 | 0.87984636 |

Table B.44 120 degree enolate complex with substrate J.






Free Energy: -3588.56440361917

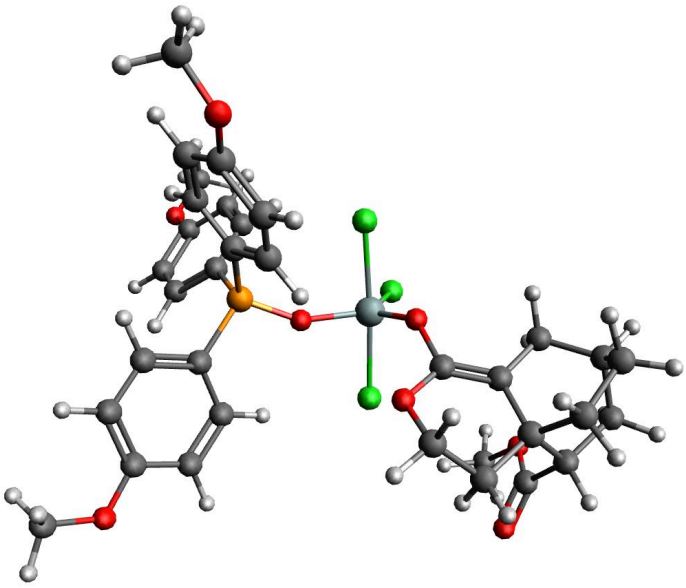
74

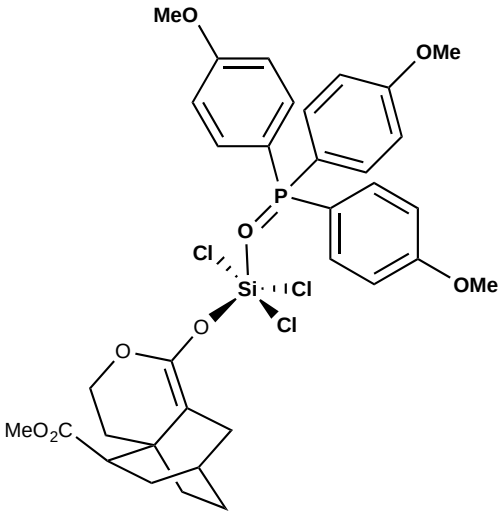
| | | | |
|---|---|---|---|
| C | -5.23247624 | -1.03168272 | -2.89767432 |
| C | -4.49313121 | -1.44568849 | -1.64055665 |
| C | -4.65710349 | 0.26087211 | -3.48965317 |
| C | -4.73977626 | -2.83475445 | -1.09751723 |
| O | -3.41149187 | 0.70954741 | -1.44095004 |
| H | -5.35081013 | 0.71048696 | -4.21183360 |
| H | -3.71842788 | 0.04909680 | -4.01675423 |
| C | -4.37356166 | 1.24385912 | -2.36106523 |
| H | -5.29558715 | 1.47289492 | -1.80515327 |

| | | | |
|---|---|---|---|
| H | -3.93817154 | 2.18128439 | -2.71845700 |
| C | -3.63848763 | -0.58662428 | -1.05664319 |
| O | -2.93808671 | -0.86195652 | 0.07179332 |
| H | -3.92790201 | -3.13672016 | -0.42840220 |
| H | -6.30722448 | -0.90296194 | -2.69160251 |
| H | -5.16549692 | -1.84126198 | -3.63962622 |
| C | -6.07734343 | -3.00066577 | -0.33841353 |
| P | 1.28917445 | 0.26429797 | 0.62926070 |
| O | -0.14554398 | -0.33877935 | 0.77880550 |
| C | 2.34589184 | -0.66977094 | -0.48616457 |
| C | 1.08985583 | 1.95201063 | 0.03442925 |
| C | 1.14620681 | 0.40964250 | 3.39110843 |
| C | 3.38625240 | 0.15875534 | 2.49309887 |
| C | 3.91636557 | 0.19770549 | 3.78480314 |
| C | 1.66587135 | 0.44905963 | 4.67490778 |
| C | 3.05282885 | 0.34065257 | 4.88184181 |
| H | 4.98743972 | 0.10067398 | 3.92095807 |
| H | 1.01384943 | 0.54093785 | 5.53801067 |
| O | 3.45827635 | 0.37247965 | 6.17679218 |
| C | 2.81650518 | -0.11338668 | -1.68992299 |
| C | 2.62282171 | -2.01570258 | -0.20247403 |
| C | 3.33431970 | -2.80359388 | -1.10355890 |
| C | 3.53490315 | -0.88758396 | -2.58822546 |
| H | 2.60255901 | 0.92289278 | -1.93143361 |
| H | 2.25595628 | -2.47095260 | 0.71349757 |
| C | 3.78270876 | -2.24277154 | -2.31047607 |
| H | 3.50969201 | -3.84679987 | -0.86834197 |
| O | 4.45767164 | -2.92557032 | -3.26880363 |
| H | 3.88861317 | -0.47461762 | -3.52777981 |
| C | 0.04277166 | 2.26172078 | -0.85785545 |
| C | 1.96658188 | 2.96374018 | 0.44594978 |
| H | -0.65858864 | 1.49357438 | -1.17193430 |
| C | -0.10126266 | 3.55766145 | -1.33082356 |
| C | 0.78725519 | 4.56795637 | -0.92177066 |
| C | 1.82666107 | 4.26864152 | -0.02822651 |
| H | 2.51653285 | 5.03307730 | 0.31007189 |
| H | 2.76348162 | 2.74707790 | 1.15204123 |
| H | -0.90530841 | 3.81450387 | -2.01306837 |
| O | 0.55559147 | 5.80235133 | -1.43801213 |
| C | 1.39179610 | 6.88540977 | -1.03929949 |
| H | 1.00098772 | 7.76332399 | -1.55538176 |
| H | 2.43274164 | 6.71522350 | -1.34198771 |
| H | 1.34081162 | 7.04369118 | 0.04501715 |
| C | 4.62956704 | -4.33482145 | -3.12396568 |
| H | 5.12290663 | -4.66370699 | -4.03948632 |
| H | 3.66134975 | -4.83995466 | -3.02417110 |

| | | | |
|---|---|---|---|
| H | 5.26521156 | -4.57020915 | -2.26147311 |
| C | 4.84641570 | 0.24434893 | 6.47108704 |
| H | 5.24300047 | -0.70964372 | 6.10247824 |
| H | 4.91954819 | 0.27296000 | 7.55894290 |
| H | 5.41988127 | 1.07537875 | 6.04170963 |
| C | 2.00544936 | 0.26453717 | 2.28162049 |
| H | 4.06203752 | 0.02821325 | 1.65175544 |
| H | 0.07112355 | 0.45094861 | 3.24482881 |
| Si | -1.41013420 | -1.46109841 | 0.38631319 |
| Cl | -1.94272857 | -1.46036120 | 2.53421394 |
| Cl | -0.91529376 | -3.52498313 | 0.43533866 |
| Cl | -0.78174624 | -1.33966704 | -1.78076302 |
| H | -4.72526090 | -3.54718617 | -1.93670814 |
| H | -6.91556823 | -2.73580214 | -0.99944213 |
| C | -6.15263520 | -2.17914457 | 0.95384722 |
| H | -6.20200679 | -4.06697523 | -0.10036611 |
| H | -6.07363163 | -1.10508880 | 0.74972476 |
| H | -5.33092046 | -2.43945978 | 1.63148959 |
| H | -7.09889680 | -2.35240923 | 1.48213272 |

Table B.45 120 degree enolate complex with substrate K.






-3931.97189445182

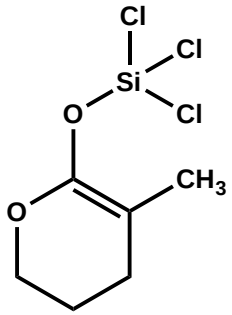
85

| | | | |
|---|---|---|---|
| C | -0.30920329 | 0.37275548 | -0.84961450 |
| C | 0.97755782 | -0.38964783 | -0.58324428 |
| C | -0.01094040 | 1.86326286 | -1.08739120 |
| C | 0.80860221 | -1.89292984 | -0.47350972 |
| O | 2.31491475 | 1.60269533 | -0.35687948 |

| | | | |
|---|---|---|---|
| H | -0.91338914 | 2.46736408 | -0.91892967 |
| H | 0.30245500 | 2.03577034 | -2.12085439 |
| C | 1.10013777 | 2.34386816 | -0.15836770 |
| H | 0.81233116 | 2.25052527 | 0.89920251 |
| H | 1.36546816 | 3.38565094 | -0.35646187 |
| C | 2.14430055 | 0.24664264 | -0.40750780 |
| O | 3.30183712 | -0.40740211 | -0.13648066 |
| H | 1.34087739 | -2.27599916 | 0.40678858 |
| C | -1.25197595 | 0.16759249 | 0.37338090 |
| C | -1.06081560 | -0.30985288 | -2.06260029 |
| C | -0.70359362 | -2.18202481 | -0.36300379 |
| P | 7.13104051 | 1.39500044 | -0.36013027 |
| O | 5.85428060 | 0.67630977 | -0.90896126 |
| C | 8.62119263 | 0.54955304 | -0.91563496 |
| C | 7.05377806 | 3.05229440 | -1.06821305 |
| C | 5.89181492 | 1.79582897 | 2.08572279 |
| C | 8.28065667 | 1.39622390 | 2.19110627 |
| C | 8.25181240 | 1.54312196 | 3.58050504 |
| C | 5.85555088 | 1.94332484 | 3.46160379 |
| C | 7.03416411 | 1.81300232 | 4.21993106 |
| H | 9.17061693 | 1.43110211 | 4.14455346 |
| H | 4.92079881 | 2.13363023 | 3.97946624 |
| O | 6.88864080 | 1.96067234 | 5.56190583 |
| C | 9.52726325 | 1.16661672 | -1.80062654 |
| C | 8.84329577 | -0.78390034 | -0.53124289 |
| C | 9.93896212 | -1.49204341 | -1.02002594 |
| C | 10.62546706 | 0.46918571 | -2.28316039 |
| H | 9.36604363 | 2.19033177 | -2.12408078 |
| H | 8.14203514 | -1.28377366 | 0.13143326 |
| C | 10.83372473 | -0.86827050 | -1.90407989 |
| H | 10.07241417 | -2.52532023 | -0.72138568 |
| O | 11.91877507 | -1.47265973 | -2.44897825 |
| H | 11.32627355 | 0.93200425 | -2.97110957 |
| C | 6.26064608 | 3.29420847 | -2.20731123 |
| C | 7.77554560 | 4.10888547 | -0.49708961 |
| H | 5.66501677 | 2.49300306 | -2.63610685 |
| C | 6.21303907 | 4.56467266 | -2.76369107 |
| C | 6.94648879 | 5.61937183 | -2.19331853 |
| C | 7.73088959 | 5.38887057 | -1.05161746 |
| H | 8.29290063 | 6.18893358 | -0.58357979 |
| H | 8.37239597 | 3.94823136 | 0.39733966 |
| H | 5.59778336 | 4.76697452 | -3.63500774 |
| O | 6.82447964 | 6.82272991 | -2.81048615 |
| C | 7.50348844 | 7.95318948 | -2.27006158 |
| H | 7.24539395 | 8.78868672 | -2.92225227 |
| H | 8.59080381 | 7.80544022 | -2.27824803 |

| | | | |
|---|---|---|---|
| H | 7.16481724 | 8.16710685 | -1.24861393 |
| C | 12.16033711 | -2.84980855 | -2.16089984 |
| H | 13.05611429 | -3.11348107 | -2.72444868 |
| H | 11.32088662 | -3.47420329 | -2.48958931 |
| H | 12.34178539 | -3.00399058 | -1.09016286 |
| C | 8.02248946 | 1.77220900 | 6.40428449 |
| H | 8.42853342 | 0.75855544 | 6.29702473 |
| H | 7.65812887 | 1.91396714 | 7.42266548 |
| H | 8.80497421 | 2.51052204 | 6.18778154 |
| C | 7.11117302 | 1.51908290 | 1.43384165 |
| H | 9.22637604 | 1.17028195 | 1.70661115 |
| H | 4.96933988 | 1.86779084 | 1.51617141 |
| Si | 4.71744025 | -0.62979182 | -1.00012231 |
| H | 1.22869482 | -2.41198591 | -1.34638398 |
| Cl | 5.18954289 | -2.39930790 | -2.07042553 |
| Cl | 3.97532326 | 0.32523370 | -2.87389836 |
| Cl | 5.58753859 | -1.52750823 | 0.87014288 |
| H | -1.98416552 | 0.26101610 | -2.21343567 |
| C | -1.39900461 | -1.78763871 | -1.68200509 |
| C | -0.31470070 | -0.14945469 | -3.38209293 |
| H | -1.09181656 | -2.46499991 | -2.48292637 |
| H | -2.48576102 | -1.89567919 | -1.56933121 |
| C | -1.29909763 | -1.33190491 | 0.77715570 |
| H | -0.86507196 | -3.24927538 | -0.16604084 |
| H | -0.72753348 | -1.50030101 | 1.69882051 |
| H | -2.33182626 | -1.64161836 | 0.98366730 |
| H | -2.25418580 | 0.54020356 | 0.11505689 |
| H | -0.89670031 | 0.77849866 | 1.21108508 |
| O | -0.39450541 | 0.84673831 | -4.08064499 |
| O | 0.43985842 | -1.21310977 | -3.71256049 |
| C | 1.20806033 | -1.10288047 | -4.92720087 |
| H | 1.95207233 | -0.31110697 | -4.82542635 |
| H | 0.54837961 | -0.89308053 | -5.77367989 |
| H | 1.69920681 | -2.06951794 | -5.04318158 |

Table B.46 Trichlorosilyl enolate from alpha-methylene delta-valerolactone.

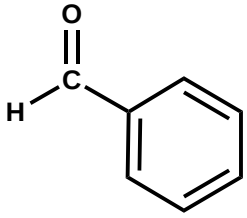



-2054.78133583200

21

| | | | |
|---|---|---|---|
| C | -6.62550764 | -1.34497628 | -1.41492222 |
| C | -5.69616668 | -0.24967063 | -1.89682457 |
| C | -6.95354378 | -1.20617809 | 0.07961037 |
| C | -5.48596964 | -0.10499225 | -3.37974911 |
| O | -5.20374463 | 0.46506685 | 0.35938754 |
| H | -7.34426905 | -2.14640093 | 0.48764764 |
| H | -7.72434785 | -0.43960429 | 0.22915900 |
| C | -5.70313731 | -0.79524124 | 0.84766026 |
| H | -4.90610165 | -1.54400334 | 0.73874078 |
| H | -5.89505017 | -0.62940737 | 1.90996843 |
| C | -5.11050691 | 0.55410390 | -0.99794881 |
| O | -4.33565746 | 1.62711996 | -1.35732554 |
| H | -4.73864202 | 0.65609519 | -3.61676537 |
| H | -6.17550928 | -2.32979626 | -1.61820379 |
| H | -7.55506068 | -1.31682476 | -2.00158538 |
| H | -5.15583362 | -1.05700985 | -3.82018151 |
| Si | -3.19334165 | 2.43736835 | -0.49827734 |
| Cl | -2.29912300 | 3.66133073 | -1.87650490 |
| Cl | -3.99460572 | 3.59597521 | 0.98886026 |
| Cl | -1.78788671 | 1.16675409 | 0.29470168 |
| H | -6.42227457 | 0.17023101 | -3.88699744 |

Table B.47 Benzaldehyde (PhCHO)



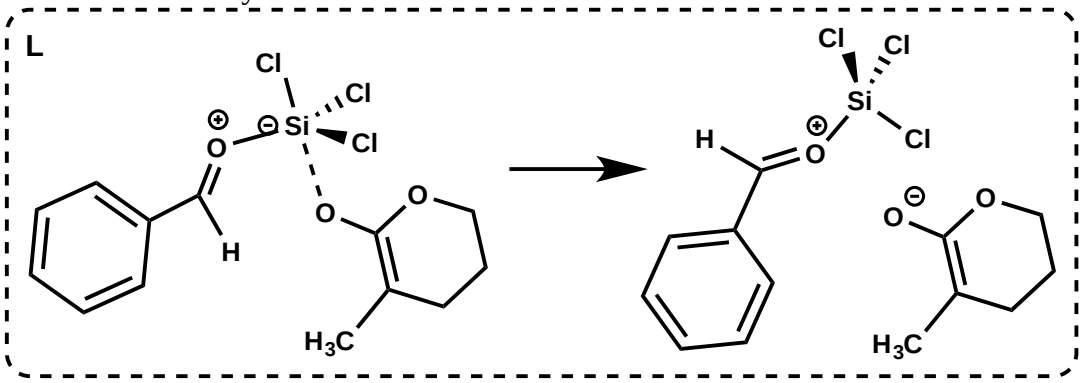

-345.588863208257

14

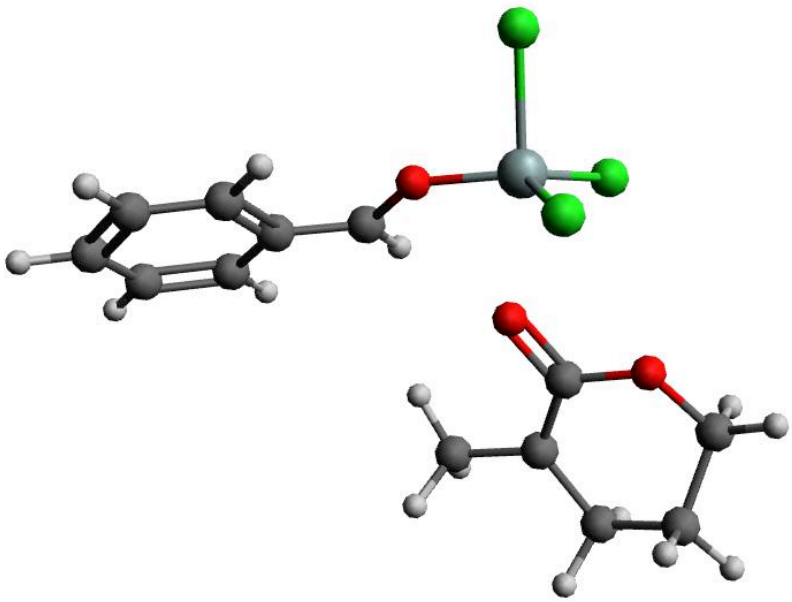
| | | | |
|---|---|---|---|
| C | -2.33795922 | 1.32850878 | 0.11825864 |
| C | -2.42170965 | 2.71217164 | -0.09104224 |
| C | -1.25967208 | 3.47715289 | -0.22885218 |
| C | -1.09330200 | 0.70824197 | 0.18915659 |
| H | -3.39527864 | 3.19286165 | -0.14623786 |
| H | -3.24563871 | 0.74028431 | 0.22513900 |
| C | 0.07791973 | 1.47221911 | 0.05135745 |
| H | -1.00386722 | -0.36231292 | 0.34970812 |
| C | -0.01140530 | 2.85639089 | -0.15745597 |
| H | -1.32808173 | 4.54951737 | -0.39104766 |
| C | 1.41224158 | 0.83416179 | 0.12108744 |

| | | | |
|---|---|---|---|
| H | 0.89942579 | 3.44284419 | -0.26401423 |
| O | 1.61104932 | -0.35576226 | 0.29186886 |
| H | 2.26973813 | 1.53200060 | 0.00321404 |

Table B.48 Pathway L transition state.




Starting E: -2400.364707
TS E: -2400.307354
Ending E: -2400.319874

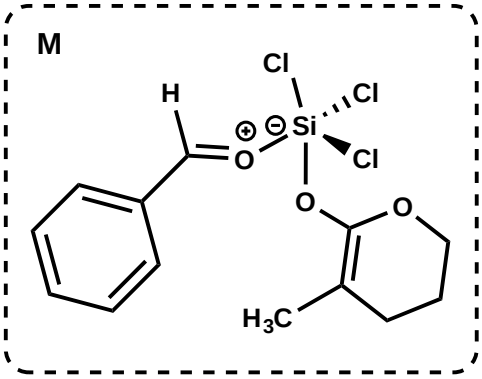


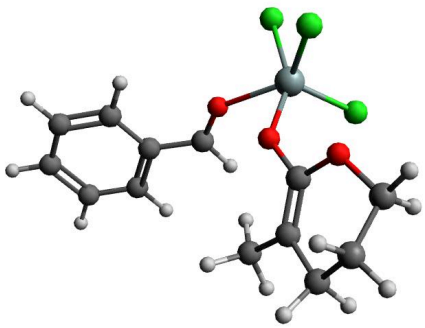
TS-L
35

C -2.485331 -3.010380 0.364082
C -3.751790 -2.445357 0.140892
C -3.861778 -1.076109 -0.150198
C -1.341231 -2.230295 0.290096
H -4.643101 -3.063858 0.196018
H -2.393471 -4.068621 0.590064

C -1.436386 -0.843878 -0.015799
H -0.361966 -2.664932 0.461017
C -2.726722 -0.281629 -0.226473
H -4.841172 -0.634505 -0.316445
C -0.291886 -0.025985 -0.119657
H -2.816909 0.778481 -0.449196
O 0.911062 -0.520595 0.129983
H -0.359752 1.032972 -0.355204
C 1.481758 2.321099 -5.279936
C 1.027608 1.680181 -3.998151
C 2.938632 1.977430 -5.609389
C -0.437958 1.622567 -3.718664
O 3.286050 1.149053 -3.336590
H 3.344732 2.657357 -6.367920
H 3.008982 0.956959 -6.009291
C 3.768570 2.068844 -4.339509
H 3.740702 3.081694 -3.915342
H 4.811411 1.782818 -4.494997
C 1.955243 1.070566 -3.109947
O 1.592610 0.387437 -2.109515
H -0.648863 1.247844 -2.717521
H 1.364908 3.415546 -5.195395
H 0.813094 2.022349 -6.100250
H -0.904501 2.612586 -3.835666
Si 2.519294 -0.143336 -0.162023
Cl 3.184632 -0.702032 1.769412
Cl 3.595508 -1.509104 -1.285368
Cl 3.063631 1.866634 -0.118083
H -0.946657 0.959738 -4.438346

Table B.49 Pathway M transition state.



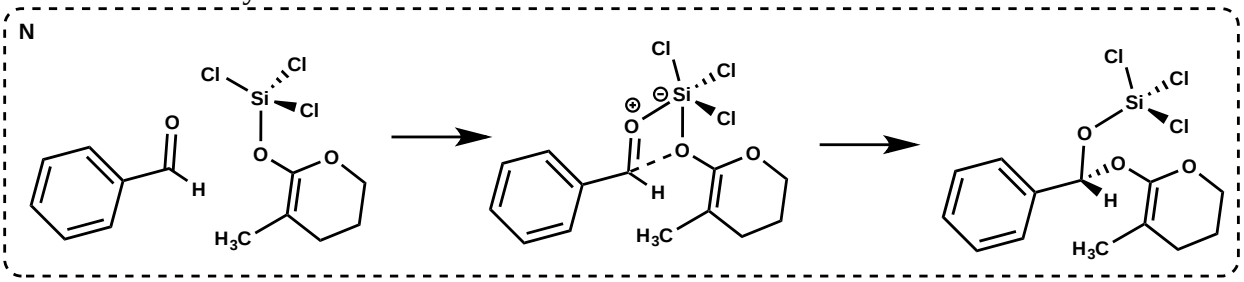
Starting E: -2400.363171
TS E: -2400.327411
Ending E: -2400.332610

TS-M

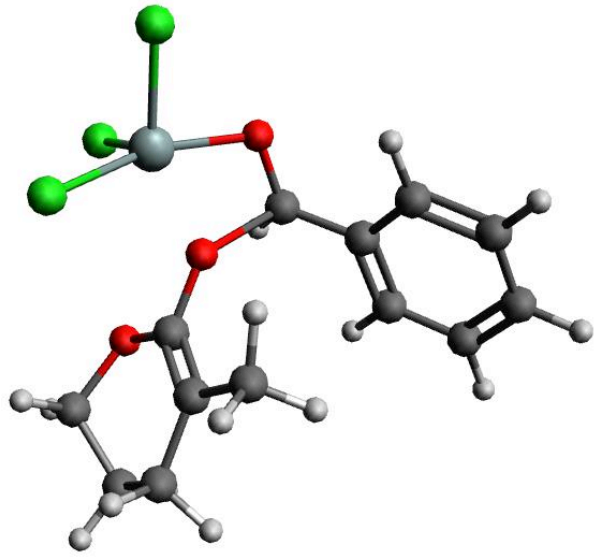
35

C -2.560894 -3.038559 0.266381
C -3.840237 -2.466729 0.221576
C -3.997411 -1.083804 0.079355
C -1.435774 -2.230348 0.160062
H -4.718911 -3.103682 0.300437
H -2.445171 -4.110919 0.387400
C -1.587136 -0.837678 0.016049
H -0.435449 -2.652338 0.186695
C -2.872154 -0.266434 -0.017561
H -4.991774 -0.648744 0.046020
C -0.420264 0.023876 -0.122484
H -2.982377 0.810540 -0.128689
O 0.731049 -0.417547 -0.166576
H -0.590219 1.109946 -0.182472
C 1.430270 1.765943 -5.447862
C 1.154141 1.253517 -4.050387
C 2.842624 1.388450 -5.916060
C -0.257826 1.313931 -3.537140
O 3.468397 0.719183 -3.657252
H 3.156592 2.004745 -6.768526
H 2.871857 0.338576 -6.239329
C 3.817836 1.572519 -4.759540
H 3.813341 2.611637 -4.406075
H 4.840503 1.290539 -5.020408
C 2.154273 0.743616 -3.304733
O 1.921190 0.126712 -2.115568
H -0.253891 1.247470 -2.447532
H 1.304375 2.860161 -5.478122
H 0.679456 1.362433 -6.145338
H -0.738564 2.264425 -3.813869
Si 2.710695 0.216627 -0.615956
Cl 2.832203 -0.324943 1.459091
Cl 4.464578 -0.804650 -1.136942
Cl 2.935622 2.286114 -0.420906
H -0.890551 0.504141 -3.933960

Table B.50 Pathway N transition state.



Starting E: -2400.366613
TS E: -2400.332750
Ending E: -2400.364740

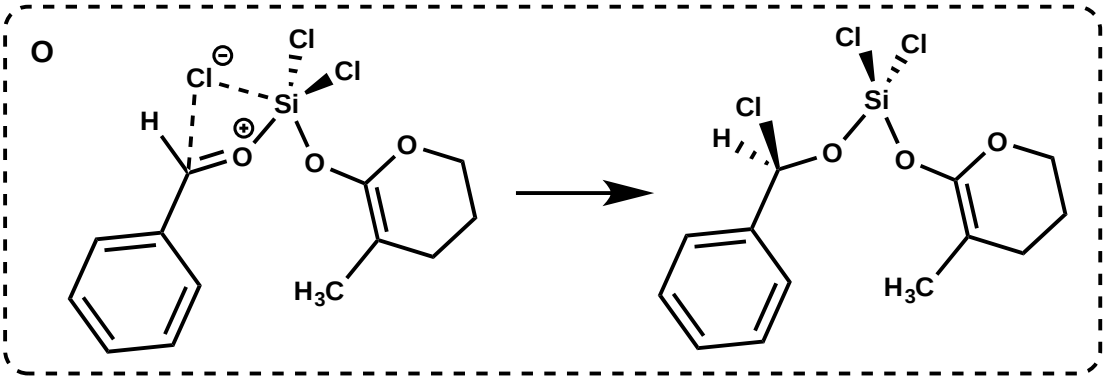


TS-N
35

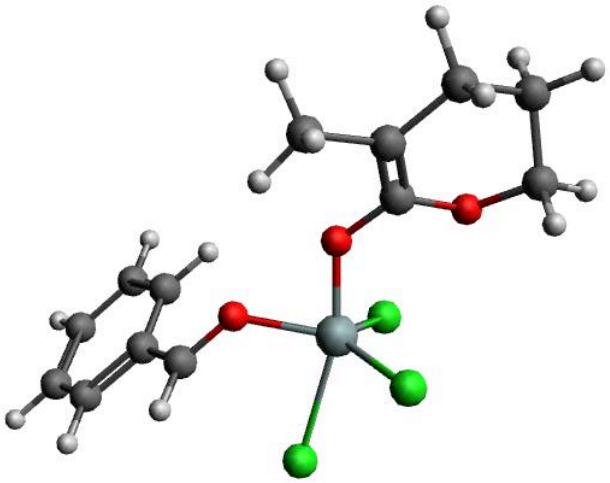
C -0.688938 -2.927541 0.124297
C -1.416192 -2.318580 1.154548
C -0.993097 -1.098804 1.692979
C 0.469207 -2.325782 -0.361341
H -2.316668 -2.793043 1.534915
H -1.025650 -3.868680 -0.301929
C 0.898623 -1.101724 0.178339
H 1.046910 -2.780784 -1.159775
C 0.159405 -0.486705 1.201123
H -1.563080 -0.625986 2.488118
C 2.127378 -0.464885 -0.294008
H 0.491467 0.464321 1.610503
O 2.738160 -0.920266 -1.364010
H 2.267818 0.588921 -0.033118
C 4.052186 -1.261341 4.390194
C 3.696942 -1.662156 2.974373
C 4.410183 0.227181 4.505553
C 3.132156 -3.040487 2.759546
O 4.463826 0.448545 2.081278
H 4.980841 0.422550 5.421496
H 3.497732 0.836016 4.548092
C 5.220745 0.659224 3.288602
H 6.157042 0.090366 3.207858
H 5.452999 1.725966 3.295709

C 3.926583 -0.798788 1.965350
O 3.566958 -1.065913 0.678806
H 3.177147 -3.345849 1.711711
H 4.893809 -1.886849 4.728291
H 3.214689 -1.500143 5.061193
H 3.688329 -3.777157 3.355145
Si 4.502178 -1.034289 -0.947107
Cl 4.783500 -2.190337 -2.683207
Cl 5.049391 0.939025 -1.315907
Cl 6.206911 -1.821842 0.075100
H 2.081092 -3.090851 3.083347

Table B.51 Pathway O transition state.




Starting E: -2400.364746
TS E: -2400.324379
Ending E: -2400.364895

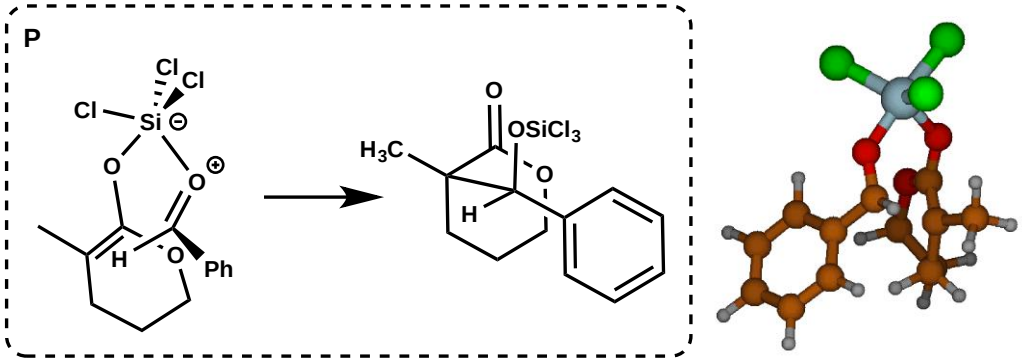


TS-O
35

C -1.187455 -3.370245 -0.119620
C -2.265974 -3.259492 0.770223

C -2.419643 -2.123358 1.577974
C -0.247479 -2.352472 -0.196326
H -2.993500 -4.064741 0.834597
H -1.082887 -4.253533 -0.742857
C -0.386872 -1.211985 0.626361
H 0.601394 -2.420282 -0.868865
C -1.485346 -1.096705 1.504893
H -3.261087 -2.049323 2.260377
C 0.614883 -0.184106 0.611328
H -1.579209 -0.217090 2.137632
O 1.596622 -0.237706 -0.195437
H 0.472955 0.711046 1.219112
C 5.833557 0.995231 -4.260293
C 4.635421 0.962662 -3.334480
C 6.843351 -0.122256 -3.950086
C 3.499902 1.900501 -3.639594
O 5.624209 -0.734202 -1.942745
H 7.839547 0.123048 -4.339588
H 6.528365 -1.060709 -4.423873
C 6.910267 -0.341972 -2.444293
H 7.218756 0.577186 -1.925952
H 7.587153 -1.153299 -2.164762
C 4.601925 0.099006 -2.303229
O 3.504288 -0.092645 -1.536433
H 2.711834 1.842845 -2.884914
H 6.321832 1.981722 -4.199090
H 5.493161 0.901868 -5.303338
H 3.851810 2.942370 -3.687714
Si 3.386880 -0.305833 0.150467
Cl 2.657760 -0.217181 2.365260
Cl 3.842586 -2.334452 0.313482
Cl 4.846932 1.132553 0.656791
H 3.046923 1.677465 -4.618141

Table B.52 Pathway P transition state.



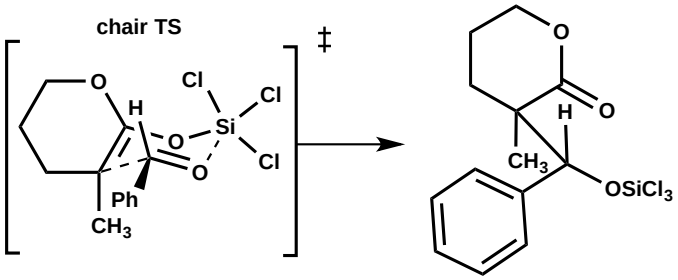

Starting E: -2400.363025
TS E: -2400.342417

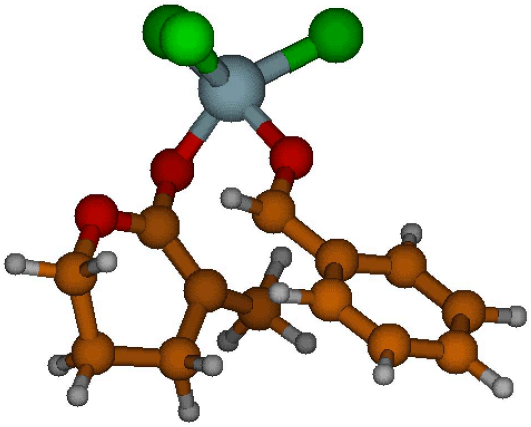
Ending E: -2400.388529

TS-P
35

C -1.219851 -3.268371 0.032160
C -2.247400 -2.853621 0.889428
C -2.199965 -1.581807 1.467805
C -0.147283 -2.419173 -0.243207
H -3.086824 -3.513225 1.092440
H -1.262832 -4.248334 -0.435593
C -0.089933 -1.142601 0.340771
H 0.639708 -2.723184 -0.925098
C -1.127692 -0.730231 1.192050
H -3.001338 -1.248295 2.121711
C 1.011178 -0.202364 0.018805
H -1.101084 0.265531 1.631005
O 1.631485 -0.440587 -1.121693
H 0.798902 0.848735 0.237971
C 1.885057 -0.960830 2.878298
C 2.388872 -0.251193 1.618500
C 2.685927 -2.238714 3.166763
C 2.664912 1.234321 1.810651
O 3.426350 -2.294037 0.822149
H 2.189479 -2.846469 3.931994
H 3.686051 -1.990464 3.546083
C 2.811786 -3.062052 1.897702
H 1.831717 -3.380075 1.528535
H 3.460487 -3.933799 2.008401
C 3.262909 -0.982624 0.775419
O 3.871073 -0.425297 -0.219192
H 3.044707 1.725292 0.914461
H 0.820630 -1.203153 2.788419
H 1.973413 -0.271565 3.726669
H 1.746868 1.750596 2.116655
Si 3.192776 0.227956 -1.739764
Cl 5.199358 0.855206 -2.209659
Cl 2.937826 -0.959730 -3.445422
Cl 2.375710 2.183043 -1.807923
H 3.401032 1.376352 2.611776

Table B.53 Pathway P transition state (minor product).



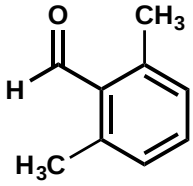
Transition State Energy: -2400.340019

35

H 1.997685 -0.972662 0.510765
C 2.072121 0.117665 0.428465
O 2.682019 0.587145 -0.632154
C 0.895844 0.868105 0.906219
C 2.998004 -0.041091 3.392422
C 3.508884 0.441441 2.040721
C 3.683219 -1.345539 3.822188
C 3.765409 1.927105 1.925667
O 4.374206 -1.752606 1.501173
H 3.160465 -1.809299 4.666603
H 4.712558 -1.146401 4.146191
C 3.707639 -2.319824 2.657269
H 2.693850 -2.597672 2.344623
H 4.266009 -3.232438 2.873066
C 4.284741 -0.441718 1.269130
O 4.880861 -0.066356 0.182739
H 4.021578 2.234417 0.910786
H 1.907909 -0.171737 3.370403
H 3.184388 0.741799 4.137482
H 2.884740 2.489069 2.251372
Si 4.165047 -0.014894 -1.482302

Cl 3.582276 1.334429 -3.019939
Cl 6.186623 -0.092613 -2.176516
Cl 3.468999 -1.942449 -1.904384
H 4.599724 2.211931 2.581404
C 0.694854 2.210358 0.537923
C -0.074493 0.216229 1.686116
C -1.214359 0.898579 2.114085
H 1.409782 2.694714 -0.118203
C -0.436160 2.892751 0.981661
H 0.044165 -0.838480 1.925858
C -1.392109 2.242073 1.771312
H -1.965668 0.380133 2.703649
H -0.587319 3.928332 0.689588
H -2.270868 2.781495 2.113281

Table B.54 2,6-dimethylbenzaldehyde

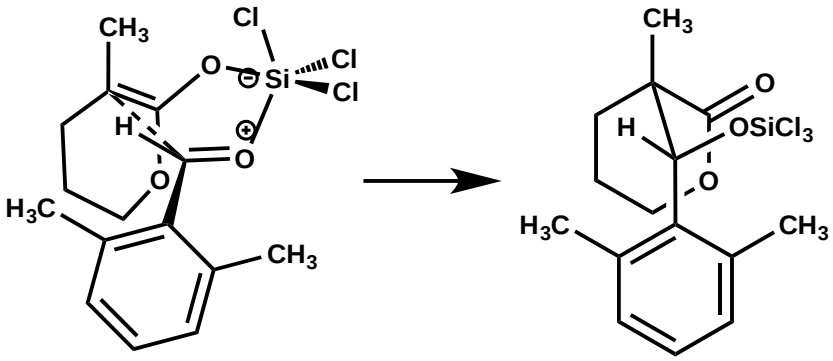


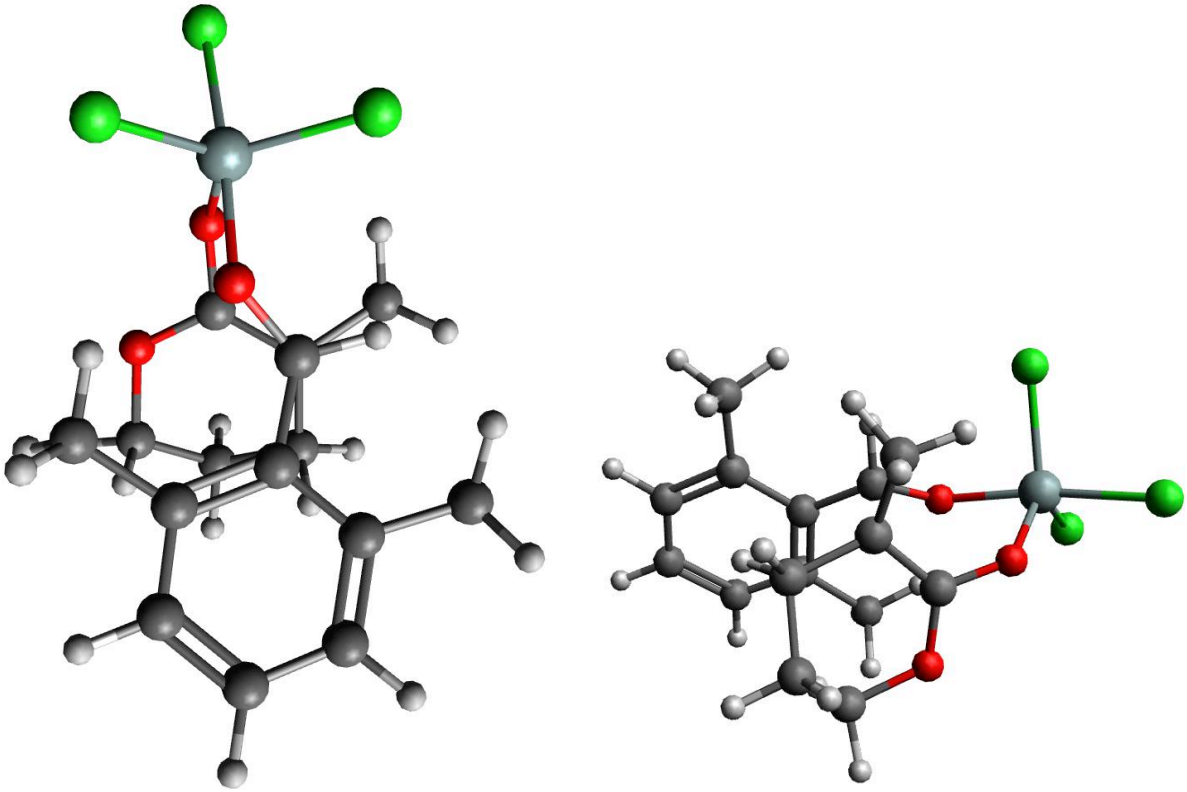

Free Energy: -424.218975738082

20

| | | | |
|---|---|---|---|
| C | -2.22797018 | -1.90816648 | 0.88296277 |
| C | -3.49318053 | -1.48239023 | 1.28372009 |
| C | -3.64080737 | -0.72584014 | 2.44616073 |
| C | -1.08467385 | -1.59304542 | 1.62720932 |
| H | -4.36638092 | -1.74019051 | 0.68917746 |
| H | -2.12024659 | -2.49721564 | -0.02469509 |
| C | -1.24130057 | -0.82005134 | 2.81179761 |
| C | 0.25486776 | -2.08790763 | 1.13551693 |
| C | -2.53104130 | -0.38362366 | 3.22395823 |
| H | -4.62990271 | -0.39640525 | 2.75510426 |
| C | -0.07703898 | -0.44518436 | 3.64513664 |
| C | -2.76299580 | 0.44091298 | 4.47779824 |
| O | 1.08985923 | -0.74680504 | 3.43757333 |
| H | -0.31342114 | 0.16861841 | 4.53393733 |
| H | -2.43963942 | -0.08174328 | 5.38585744 |
| H | -3.83000867 | 0.65718576 | 4.58925748 |
| H | -2.23611558 | 1.40188442 | 4.44869988 |
| H | 0.95005076 | -1.26225508 | 0.95130180 |
| H | 0.12632100 | -2.65366048 | 0.20649614 |
| H | 0.74579486 | -2.72978703 | 1.87428939 |

Table B.55 Pathway P transition state with 2,6-dimethylbenzaldehyde



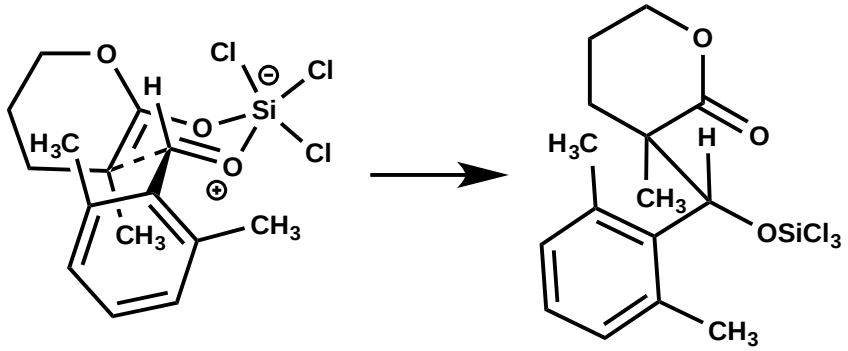
Transition State Energy: -2478.963637

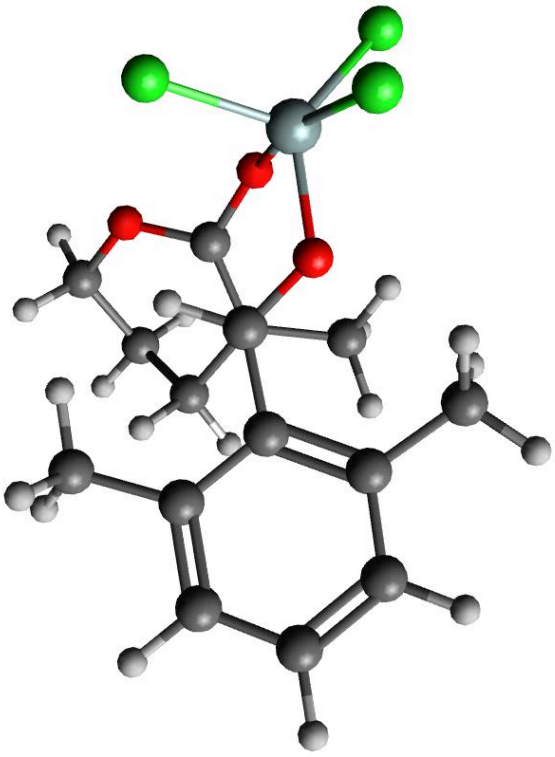
41

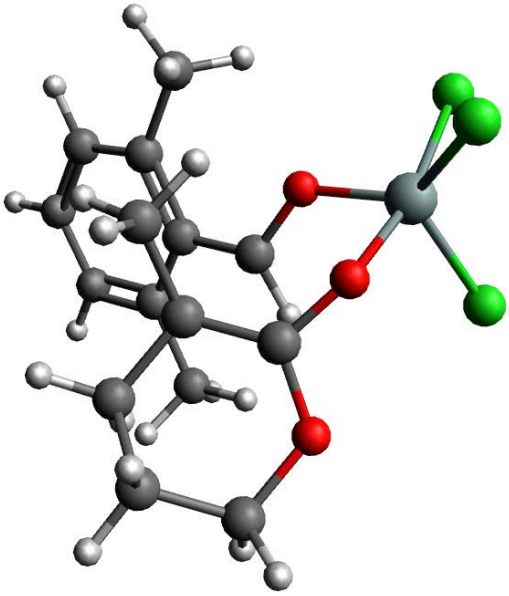
C -0.678595 -2.888809 2.755559
C -1.394085 -2.063861 3.618785
C -1.334728 -0.683988 3.442917
C 0.131233 -2.374988 1.733808
H -2.018735 -2.492402 4.398462
H -0.762795 -3.969577 2.847400
C 0.255903 -0.960250 1.609874
C 0.782011 -3.413483 0.834921
C -0.528444 -0.114102 2.450704

H -1.931054 -0.030848 4.075947
C 1.196229 -0.296218 0.669736
C -0.560547 1.401545 2.349132
O 1.601396 -0.947856 -0.395877
H 1.023648 0.767328 0.514802
C 2.756921 0.102884 3.363515
C 2.944056 0.254613 1.854193
C 3.652779 -1.001172 3.942617
C 3.175544 1.686354 1.389588
O 3.944600 -1.949769 1.694621
H 3.346999 -1.265975 4.961849
H 4.693581 -0.657763 3.992178
C 3.572466 -2.240389 3.070995
H 2.555069 -2.642791 3.046578
H 4.260693 -3.028018 3.383374
C 3.652158 -0.761810 1.182302
O 3.981559 -0.655516 -0.068265
H 3.425995 1.764003 0.331705
H 1.705384 -0.101360 3.597748
H 3.003045 1.057405 3.843162
H 2.289929 2.307665 1.569103
Si 2.970598 -0.568979 -1.528092
Cl 2.046008 1.246665 -2.114692
Cl 4.792888 -0.216863 -2.617773
Cl 2.421287 -2.278666 -2.611792
H 4.002281 2.124761 1.964443
H -0.359094 1.787009 1.347710
H 0.160633 1.868409 3.033887
H -1.552758 1.765182 2.633634
H 1.214347 -3.001626 -0.069815
H 0.027921 -4.154639 0.544743
H 1.569682 -3.962043 1.369252

Table B.56 Pathway P transition state with 2,6-dimethylbenzaldehyde (minor product).







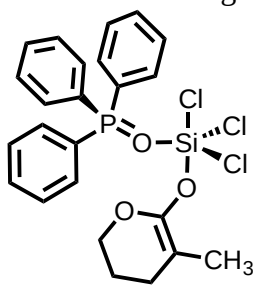
Transition State E: -2478.957301

41

H -0.526814 -1.070984 -1.172546
C -0.186602 -0.040996 -1.149829
O 0.776459 0.265874 -1.966052
C -1.116658 0.972622 -0.661933
C 0.485862 -0.882524 2.090132
C 1.215713 -0.519156 0.808222
C 1.120647 -2.165100 2.650559
C 2.006671 0.763780 0.810209
O 1.304414 -2.867847 0.276496
H 0.659229 -2.479946 3.594976
H 2.187749 -1.997112 2.842830
C 0.933575 -3.271817 1.621966
H -0.116237 -3.583090 1.589316
H 1.545666 -4.153991 1.831964
C 1.620994 -1.586126 0.007793
O 2.310279 -1.447039 -1.087597
H 2.465223 0.972218 -0.157465
H -0.581818 -1.068852 1.907461
H 0.540763 -0.057989 2.807746
H 1.373868 1.613220 1.094835

Si 1.877169 -0.884527 -2.765098
Cl 1.421851 0.197563 -4.592428
Cl 3.951138 -0.793237 -3.102617
Cl 0.868434 -2.656050 -3.246793
H 2.819534 0.705140 1.551068
C -2.340657 0.530559 -0.075754
C -0.879875 2.374233 -0.847821
C -2.768215 -0.920585 0.069642
C -3.264848 1.482913 0.365288
C -1.840562 3.276255 -0.382003
C 0.317683 2.951718 -1.573237
C -3.018268 2.844802 0.228196
H -4.199041 1.143098 0.808989
H -1.667496 4.339411 -0.519525
H -3.750808 3.570597 0.572776
H -2.068321 -1.652373 -0.330976
H -3.722438 -1.074159 -0.448562
H -2.934115 -1.172380 1.123854
H 0.374981 2.588676 -2.603948
H 1.266904 2.691465 -1.099458
H 0.238915 4.043033 -1.595540

Table B.57 90 degree enolate complex (swapped) with TPPO.



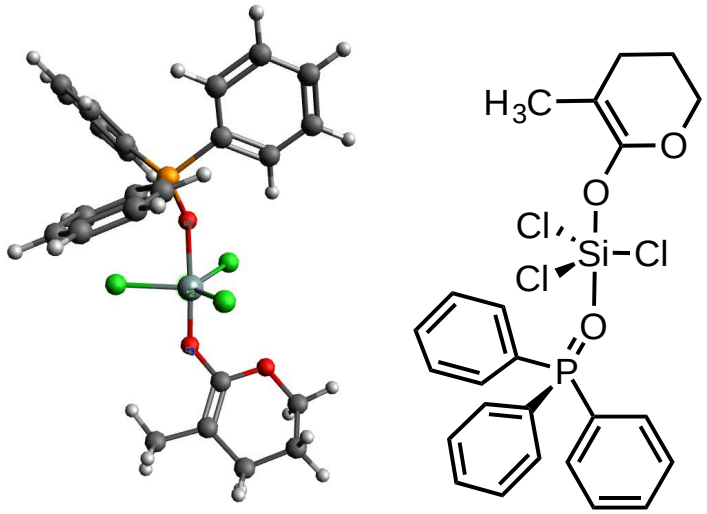

90° O-Si-O enolate free energy: -3166.34783083244

56

| | | | |
|---|---|---|---|
| C | 1.38084848 | -3.74940060 | -1.28290650 |
| C | 1.99149185 | -3.36893177 | 0.04855037 |
| C | 2.23024550 | -3.24454836 | -2.45548991 |
| C | 1.46818814 | -4.06270535 | 1.27701219 |
| O | 3.49178852 | -1.76908056 | -0.96911063 |
| H | 1.66522142 | -3.25830242 | -3.39646549 |
| H | 3.11208576 | -3.88378873 | -2.58926862 |
| C | 2.69561968 | -1.82516456 | -2.16078415 |
| H | 1.82787507 | -1.15871032 | -2.03142684 |
| H | 3.33429180 | -1.42178857 | -2.95244605 |
| C | 2.99558921 | -2.47413352 | 0.11327459 |
| O | 3.60569047 | -2.11191083 | 1.25338271 |

| | | | |
|---|---|---|---|
| H | 1.89748279 | -3.64563034 | 2.19123032 |
| H | 0.35158276 | -3.36035919 | -1.36341822 |
| H | 1.28739438 | -4.84432541 | -1.33840811 |
| H | 0.37282045 | -3.97188135 | 1.34100643 |
| P | 6.59377670 | 0.38891701 | 0.65925369 |
| O | 5.64341694 | -0.78370960 | 1.03922901 |
| C | 7.63558791 | -0.07350652 | -0.74936124 |
| C | 5.50230961 | 1.75452768 | 0.18044818 |
| C | 6.97412388 | 1.24426001 | 3.26267560 |
| C | 8.99189696 | 1.15002046 | 1.90767139 |
| C | 9.73458907 | 1.62845115 | 2.98986364 |
| C | 7.72270840 | 1.71693555 | 4.33823566 |
| C | 9.10179637 | 1.91087902 | 4.20224116 |
| H | 10.80680887 | 1.77003665 | 2.88555508 |
| H | 7.23167851 | 1.92237901 | 5.28516742 |
| H | 9.68285323 | 2.27564098 | 5.04515364 |
| C | 7.74834677 | 0.77631084 | -1.86201940 |
| C | 8.32089430 | -1.30148369 | -0.72860708 |
| C | 9.11397382 | -1.66561883 | -1.81710716 |
| C | 8.54782672 | 0.40301904 | -2.94415158 |
| H | 7.20772945 | 1.71728272 | -1.89107147 |
| H | 8.23116744 | -1.96394818 | 0.12779647 |
| C | 9.22935905 | -0.81681928 | -2.92223170 |
| H | 9.63615326 | -2.61814340 | -1.80087542 |
| H | 9.84615384 | -1.10840249 | -3.76843903 |
| H | 8.62899306 | 1.06083371 | -3.80519666 |
| C | 4.23245926 | 1.45829324 | -0.34133644 |
| C | 5.91843147 | 3.08867405 | 0.31882092 |
| H | 3.91008108 | 0.42429576 | -0.43479126 |
| C | 3.38910817 | 2.50409007 | -0.72292059 |
| C | 3.80448905 | 3.83244254 | -0.59203328 |
| C | 5.06895375 | 4.12495181 | -0.07195234 |
| H | 5.38973927 | 5.15692293 | 0.04135650 |
| H | 6.89216608 | 3.32158555 | 0.74142996 |
| H | 2.40130096 | 2.27812593 | -1.11525404 |
| H | 3.13987492 | 4.64045081 | -0.88691329 |
| C | 7.61023981 | 0.95800479 | 2.04253798 |
| H | 9.49028254 | 0.91701889 | 0.97179617 |
| H | 5.90618721 | 1.07976067 | 3.37951613 |
| Si | 5.23137347 | -2.30222297 | 1.80976572 |
| Cl | 5.54075018 | -4.11904048 | 0.75835264 |
| Cl | 4.53899472 | -2.14897429 | 3.80026617 |
| Cl | 7.37465679 | -2.40959735 | 2.56704026 |
| H | 1.69536085 | -5.13963194 | 1.25482650 |

Table B.58 180 degree enolate complex with TPPO.




180° O-Si-O enolate free energy: -3166.35329511741

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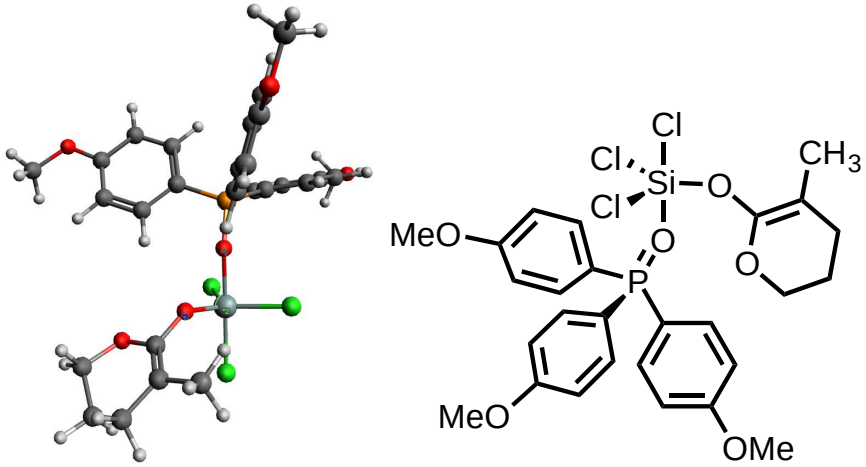
| | | | |
|---|---|---|---|
| C | -5.28479275 | -2.79719461 | -2.88585947 |
| C | -4.31042879 | -2.73172311 | -1.72986166 |
| C | -5.52116200 | -1.41356561 | -3.50603323 |
| C | -3.75073837 | -4.03142494 | -1.21793834 |
| O | -4.46643575 | -0.32853506 | -1.59010205 |
| H | -6.42508463 | -1.40254060 | -4.12866340 |
| H | -4.67426873 | -1.13762386 | -4.14763860 |
| C | -5.65092187 | -0.37956036 | -2.39460522 |
| H | -6.50287154 | -0.61982531 | -1.74031876 |
| H | -5.77857528 | 0.63606268 | -2.77933081 |
| C | -3.96611493 | -1.54243892 | -1.19774904 |
| O | -3.10084203 | -1.42409958 | -0.16953175 |
| H | -6.24289616 | -3.23448233 | -2.55670737 |
| H | -4.89588998 | -3.48489882 | -3.65247242 |
| P | 1.21956611 | 1.01353864 | 0.61518431 |
| O | -0.30173258 | 0.78632193 | 0.55427958 |
| C | 2.24030351 | -0.20017983 | -0.27424675 |
| C | 1.52904062 | 2.65831792 | -0.09852050 |
| C | 0.76617579 | 1.23165433 | 3.33881034 |
| C | 3.08836414 | 0.85835938 | 2.72724821 |
| C | 3.45120604 | 0.92570609 | 4.07349829 |
| C | 1.13602562 | 1.29573387 | 4.68336047 |
| C | 2.47599287 | 1.14596107 | 5.05099423 |
| H | 4.49186122 | 0.79674991 | 4.35889375 |
| H | 0.37444460 | 1.45307778 | 5.44210283 |
| C | 2.77253140 | 0.09992142 | -1.53840388 |
| C | 2.45012802 | -1.47290518 | 0.28503545 |

| | | | |
|---|---|---|---|
| C | 3.18520054 | -2.42903305 | -0.41514387 |
| C | 3.51123927 | -0.86028546 | -2.23182846 |
| H | 2.60723504 | 1.07609882 | -1.98321717 |
| H | 2.02965978 | -1.72028474 | 1.25437126 |
| C | 3.71720367 | -2.12353488 | -1.67165061 |
| H | 3.33681594 | -3.41355801 | 0.01864390 |
| H | 3.91871303 | -0.62232769 | -3.21054468 |
| C | 0.47365136 | 3.30645008 | -0.75579537 |
| C | 2.78010759 | 3.28615602 | 0.00950347 |
| H | -0.49388935 | 2.81979128 | -0.82592478 |
| C | 0.67556000 | 4.57368487 | -1.30935370 |
| C | 1.92260640 | 5.19427566 | -1.20667658 |
| C | 2.97506516 | 4.55053429 | -0.54611304 |
| H | 3.94439397 | 5.03432364 | -0.46022144 |
| H | 3.60006972 | 2.79583118 | 0.52752644 |
| H | -0.14466691 | 5.07311372 | -1.81769025 |
| C | 1.74415091 | 1.01693606 | 2.35533477 |
| H | 3.84861053 | 0.66299451 | 1.97563060 |
| H | -0.27547662 | 1.33071222 | 3.04938872 |
| Si | -1.80325304 | -0.36198222 | 0.13931878 |
| Cl | -2.94738271 | 1.20941121 | 0.95076385 |
| Cl | -0.98598658 | -1.74207240 | 1.52616446 |
| Cl | -1.10935923 | -0.28643655 | -1.86897238 |
| H | -4.55917953 | -4.73103186 | -0.95387193 |
| H | -3.12702716 | -3.88324953 | -0.33295781 |
| H | -3.14022435 | -4.53309940 | -1.98522113 |
| H | 2.76070793 | 1.19255882 | 6.09900846 |
| H | 2.07651098 | 6.18074460 | -1.63654901 |
| H | 4.28832910 | -2.87192812 | -2.21506671 |

Table B.59 90 degree enolate complex with 4-OMe-TPPO.

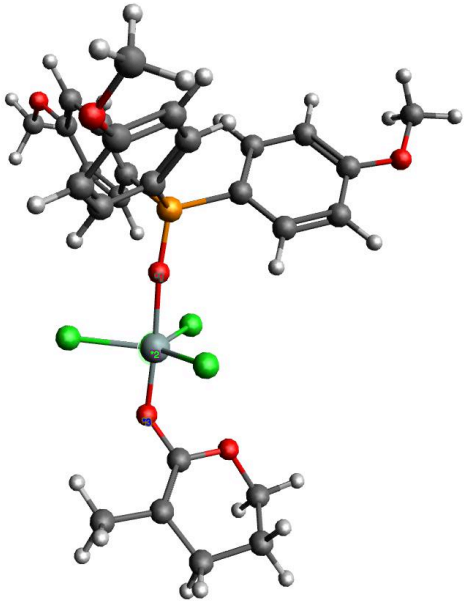


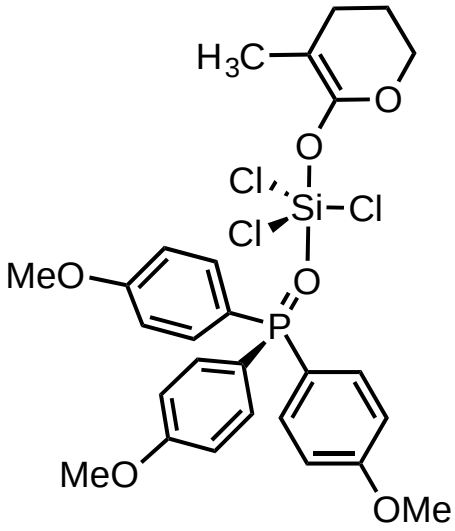

90° O-Si-O enolate free energy: -3509.94387853997

| | | | |
|---|---|---|---|
| C | 0.82039689 | -4.00795087 | 1.13722483 |
| C | 2.25707043 | -3.53275667 | 1.18602895 |
| C | 0.11053457 | -3.51983865 | -0.13287821 |
| C | 3.17381056 | -4.19872802 | 2.17545484 |
| O | 1.90621002 | -1.92871008 | -0.58656440 |
| H | -0.97973268 | -3.60503122 | -0.04079136 |
| H | 0.42065328 | -4.12450236 | -0.99388398 |
| C | 0.49167695 | -2.06837575 | -0.39501631 |
| H | 0.19293923 | -1.43174313 | 0.45263586 |
| H | 0.04016766 | -1.67423490 | -1.30972839 |
| C | 2.68538537 | -2.60213046 | 0.31700115 |
| O | 3.95552906 | -2.12790910 | 0.26098186 |
| H | 4.16213900 | -3.73294702 | 2.20209986 |
| H | 0.27299001 | -3.67507248 | 2.03478985 |
| H | 0.80464045 | -5.10749469 | 1.17014710 |
| H | 2.75040664 | -4.15801721 | 3.19070548 |
| P | 6.80670536 | 0.32733475 | -0.01606938 |
| O | 5.97290002 | -0.96535573 | 0.02619755 |
| C | 8.33287975 | 0.22542354 | -0.97762110 |
| C | 5.78168001 | 1.66725297 | -0.67087354 |
| C | 6.58070184 | 0.00336624 | 2.73854494 |
| C | 8.17871793 | 1.67822132 | 2.04054730 |
| C | 8.46225740 | 1.97941260 | 3.37413829 |
| C | 6.85454770 | 0.29596514 | 4.06753676 |
| C | 7.79581583 | 1.28574549 | 4.39573532 |
| H | 9.19806401 | 2.74299617 | 3.59900207 |
| H | 6.35344021 | -0.23480275 | 4.87137270 |
| O | 7.99380094 | 1.49499454 | 5.72433029 |
| C | 8.35111478 | 0.56345907 | -2.33818568 |
| C | 9.50275166 | -0.30570340 | -0.39603748 |
| C | 10.65533181 | -0.47031979 | -1.14820673 |
| C | 9.50552792 | 0.40280587 | -3.10410117 |
| H | 7.45374588 | 0.94153684 | -2.81719093 |
| H | 9.50789730 | -0.59939185 | 0.64934632 |
| C | 10.66533991 | -0.11563335 | -2.50875203 |
| H | 11.55856679 | -0.88262637 | -0.70929962 |
| O | 11.83978539 | -0.31283446 | -3.15988560 |
| H | 9.48375311 | 0.66920851 | -4.15445017 |
| C | 4.40296640 | 1.45727766 | -0.80325135 |
| C | 6.31406707 | 2.93101085 | -0.98984151 |
| H | 3.97391830 | 0.48832145 | -0.56654464 |
| C | 3.56518256 | 2.48113429 | -1.25090432 |
| C | 4.10652836 | 3.73434031 | -1.56820860 |
| C | 5.48935806 | 3.95404842 | -1.43395729 |
| H | 5.89023496 | 4.93047182 | -1.68847723 |

| | | | |
|---|---|---|---|
| H | 7.38157075 | 3.11687947 | -0.90352306 |
| H | 2.50450054 | 2.28294216 | -1.35289753 |
| O | 3.38449958 | 4.79651668 | -2.01461293 |
| C | 7.24299119 | 0.69205380 | 1.70499070 |
| H | 8.71322719 | 2.21851352 | 1.26318627 |
| H | 5.85729620 | -0.76708941 | 2.49107348 |
| Si | 5.25507931 | -2.51449270 | -0.74420590 |
| Cl | 4.37686055 | -4.33316847 | -1.57272747 |
| Cl | 6.93195163 | -3.53647768 | 0.05310393 |
| Cl | 5.46539926 | -1.61378732 | -2.65981635 |
| H | 3.31427299 | -5.26195370 | 1.93012146 |
| C | 11.91412765 | -0.02195726 | -4.55384802 |
| C | 8.94090786 | 2.47537638 | 6.13677076 |
| C | 1.97718509 | 4.64721076 | -2.18588107 |
| H | 8.92405966 | 2.45913352 | 7.22739599 |
| H | 8.65877059 | 3.47434840 | 5.78085937 |
| H | 9.94913627 | 2.22605945 | 5.78237048 |
| H | 12.93307137 | -0.27334860 | -4.85115329 |
| H | 11.72776821 | 1.04189704 | -4.74644288 |
| H | 11.20353402 | -0.63355650 | -5.12284760 |
| H | 1.62179597 | 5.61299531 | -2.54775937 |
| H | 1.48659868 | 4.40809556 | -1.23421514 |
| H | 1.74940672 | 3.87023207 | -2.92589213 |

Table B.60 180 degree enolate complex with 4-OMe-TPPO.






180° O-Si-O enolate free energy: -3509.93915072859

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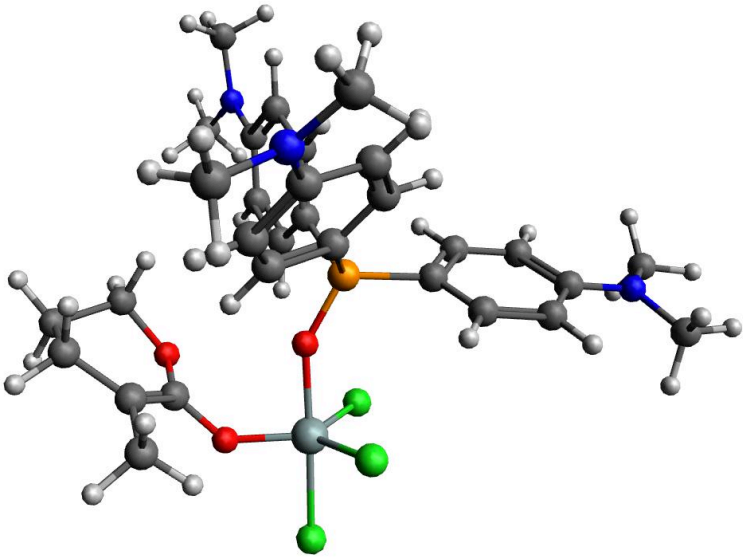
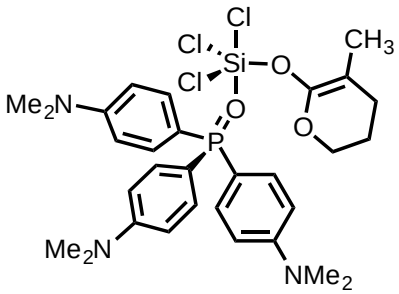
| | | | |
|---|---|---|---|
| C | -1.01639164 | 0.45204815 | -0.96595188 |
| C | 0.35126349 | 0.32782704 | -1.60152846 |
| C | -0.92550082 | 0.52605164 | 0.56451457 |
| C | 0.44731571 | 0.52749561 | -3.08985398 |
| O | 1.41061999 | -0.17798440 | 0.50621020 |
| H | -1.89365516 | 0.30803905 | 1.03405330 |
| H | -0.62577823 | 1.53428184 | 0.87803419 |
| C | 0.12036665 | -0.46771579 | 1.05606392 |
| H | -0.15656152 | -1.49383544 | 0.76914259 |
| H | 0.25640115 | -0.43066547 | 2.14058562 |
| C | 1.43298888 | 0.05777852 | -0.84444201 |
| Cl | 4.87186547 | 0.34913319 | -2.92664248 |
| H | 1.46221205 | 0.35341221 | -3.45585020 |
| H | -1.65849899 | -0.39321460 | -1.26757338 |
| H | -1.51617299 | 1.35366994 | -1.35193807 |
| H | -0.23058318 | -0.15647297 | -3.62438739 |
| P | 7.22499916 | 1.91205114 | -0.14079975 |
| O | 5.85395827 | 1.42416593 | -0.61924931 |
| C | 8.53726802 | 0.79985557 | -0.70606487 |
| C | 7.52883861 | 3.54864243 | -0.84721863 |
| C | 6.16855365 | 2.46626510 | 2.37642566 |
| C | 8.46643256 | 1.70290390 | 2.36846044 |
| C | 8.52209793 | 1.82675704 | 3.75936214 |
| C | 6.21404222 | 2.59019792 | 3.75658700 |
| C | 7.39181023 | 2.27478115 | 4.45780080 |
| H | 9.43612820 | 1.56234840 | 4.27860723 |
| H | 5.34436793 | 2.91819281 | 4.31754611 |
| O | 7.33277576 | 2.42973753 | 5.80664211 |
| C | 9.77139357 | 1.28652587 | -1.17553369 |
| C | 8.32321166 | -0.58570310 | -0.67097854 |
| C | 9.31493754 | -1.47303006 | -1.08915977 |
| C | 10.76659743 | 0.41043005 | -1.58919132 |
| H | 9.95111103 | 2.35630874 | -1.23159945 |
| H | 7.37201194 | -0.98142752 | -0.32695127 |
| C | 10.54411942 | -0.97641062 | -1.54937066 |
| H | 9.11357761 | -2.53771760 | -1.06055043 |
| O | 11.57302187 | -1.75232696 | -1.98087049 |
| H | 11.71906685 | 0.77658017 | -1.96019239 |
| C | 7.16124955 | 3.77526737 | -2.19004408 |
| C | 8.11823944 | 4.58820968 | -0.12012159 |
| H | 6.67789552 | 2.98651483 | -2.76085277 |
| C | 7.39233324 | 5.00597694 | -2.78387523 |
| C | 7.99189692 | 6.04442357 | -2.04805584 |
| C | 8.35360597 | 5.83385786 | -0.71025204 |
| H | 8.80585874 | 6.62282560 | -0.12018175 |
| H | 8.39182035 | 4.44275173 | 0.92140085 |

| | | | |
|---|---|---|---|
| H | 7.10631592 | 5.19395101 | -3.81413804 |
| O | 8.17170651 | 7.21183646 | -2.71988520 |
| C | 8.75151987 | 8.31994699 | -2.03694115 |
| H | 8.77830116 | 9.13177607 | -2.76503242 |
| H | 9.77218053 | 8.09083716 | -1.70528796 |
| H | 8.13975350 | 8.61849856 | -1.17662958 |
| C | 11.40711035 | -3.16876497 | -1.99758630 |
| H | 12.34417204 | -3.56867820 | -2.38718550 |
| H | 10.57997244 | -3.46164834 | -2.65567052 |
| H | 11.23344486 | -3.55839249 | -0.98688689 |
| C | 8.48520075 | 2.12725742 | 6.58760406 |
| H | 8.76719707 | 1.07188139 | 6.48555863 |
| H | 8.20059590 | 2.33004554 | 7.62096599 |
| H | 9.33212769 | 2.76676306 | 6.30814631 |
| C | 7.30162119 | 2.02472067 | 1.66228832 |
| H | 9.34302764 | 1.33976655 | 1.83938104 |
| H | 5.24693474 | 2.69553790 | 1.84886847 |
| Si | 4.17993445 | 0.63671376 | -0.94303767 |
| Cl | 4.70664925 | -0.84406400 | 0.48306638 |
| Cl | 3.36539719 | 2.50576776 | -0.31575479 |
| O | 2.67447909 | -0.05735177 | -1.35430620 |
| H | 0.15201580 | 1.54893546 | -3.37686202 |

Table B.61 90 degree enolate complex with 4-$NMe_2$-TPPO.






90° O-Si-O enolate free energy: -3568.27939772492

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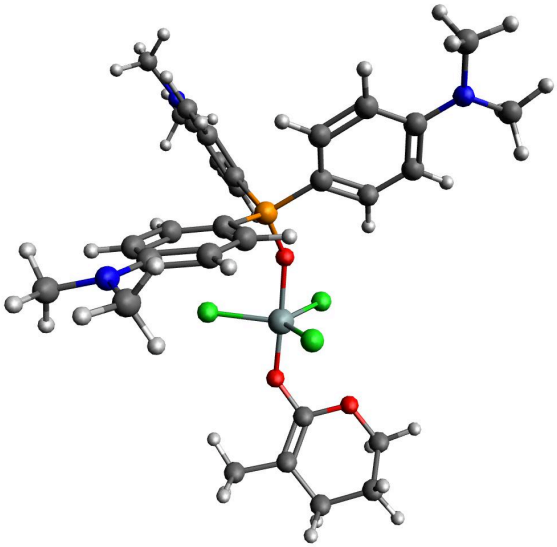
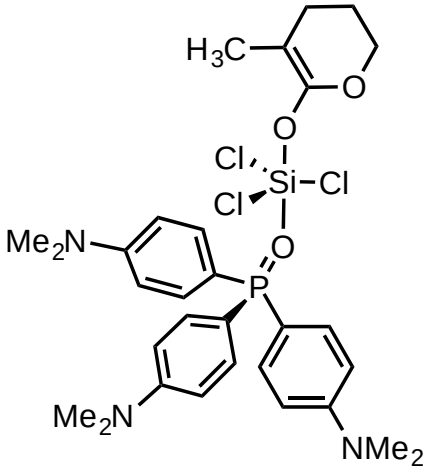
| | | | |
|---|---|---|---|
| C | 2.48525550 | -2.53204049 | -2.04406574 |
| C | 2.81052323 | -2.58262353 | -0.56537392 |

| | | | |
|---|---|---|---|
| C | 3.56732081 | -3.22773212 | -2.87964846 |
| C | 1.69525616 | -2.28256599 | 0.40059816 |
| O | 5.09366342 | -3.24987629 | -0.97480504 |
| H | 3.49471515 | -2.95268989 | -3.93977146 |
| H | 3.45321343 | -4.31725177 | -2.81223171 |
| C | 4.94058529 | -2.84506694 | -2.34158288 |
| H | 5.09391934 | -1.75785689 | -2.40274921 |
| H | 5.75247026 | -3.34275293 | -2.87868173 |
| C | 4.03977994 | -2.95410267 | -0.15345915 |
| O | 4.35076058 | -3.21147573 | 1.13315974 |
| H | 2.02187063 | -2.34560509 | 1.44113684 |
| H | 2.36230309 | -1.48771687 | -2.38007035 |
| H | 1.51146807 | -3.01403582 | -2.21901416 |
| H | 1.28033163 | -1.27523922 | 0.23637235 |
| P | 6.32252899 | 0.28230495 | 0.80484217 |
| O | 5.62114632 | -1.07508781 | 1.09971813 |
| C | 7.33143221 | 0.03840459 | -0.67353443 |
| C | 5.05424304 | 1.51931017 | 0.46586570 |
| C | 6.82655848 | 1.42670078 | 3.30632823 |
| C | 8.78276800 | 0.88384278 | 2.01027816 |
| C | 9.59889650 | 1.33203881 | 3.04024881 |
| C | 7.63061313 | 1.87347272 | 4.34408559 |
| C | 9.04574271 | 1.83829837 | 4.24347568 |
| H | 10.67262012 | 1.27115575 | 2.90975351 |
| H | 7.15176239 | 2.23753457 | 5.24492372 |
| N | 9.84900089 | 2.28235791 | 5.27271371 |
| C | 7.57973209 | 1.08066807 | -1.58040360 |
| C | 7.91537942 | -1.21438678 | -0.92666798 |
| C | 8.72912040 | -1.41458688 | -2.03502188 |
| C | 8.38789361 | 0.89113166 | -2.69525337 |
| H | 7.12750901 | 2.05723175 | -1.42781269 |
| H | 7.72012742 | -2.04495958 | -0.25597921 |
| C | 8.99720471 | -0.36464035 | -2.94968420 |
| H | 9.14968894 | -2.40106074 | -2.18977035 |
| N | 9.81599432 | -0.55707630 | -4.04425642 |
| H | 8.53875188 | 1.72362801 | -3.37222904 |
| C | 3.81250698 | 1.10644845 | -0.04710319 |
| C | 5.26959855 | 2.89450138 | 0.64863777 |
| H | 3.61231502 | 0.04689044 | -0.18139320 |
| C | 2.82528513 | 2.02830259 | -0.36653061 |
| C | 3.03719757 | 3.42079259 | -0.19686186 |
| C | 4.28965815 | 3.82781865 | 0.32889320 |
| H | 4.49881766 | 4.87632266 | 0.50446385 |
| H | 6.20933306 | 3.24883193 | 1.06343463 |
| H | 1.87796842 | 1.65816406 | -0.73924931 |
| N | 2.06353289 | 4.34031279 | -0.53235447 |

| | | | |
|---|---|---|---|
| C | 7.38224897 | 0.91883682 | 2.11689998 |
| H | 9.24926817 | 0.49177854 | 1.11181081 |
| H | 5.74921496 | 1.45399310 | 3.43368791 |
| Si | 5.25745247 | -2.44513721 | 2.32158294 |
| Cl | 4.82817373 | -4.09057046 | 3.68253430 |
| Cl | 4.25971717 | -1.01736541 | 3.55120763 |
| Cl | 7.36225896 | -2.70013285 | 2.53698048 |
| H | 0.86049288 | -2.98787950 | 0.26762286 |
| C | 0.73004779 | 3.88231813 | -0.89719698 |
| C | 2.25053053 | 5.74567134 | -0.20263577 |
| C | 11.29054524 | 2.09139392 | 5.19736573 |
| C | 9.25666888 | 2.61156344 | 6.56295984 |
| C | 9.95292019 | 0.49194784 | -5.04321555 |
| C | 10.31478465 | -1.89007854 | -4.35118371 |
| H | 9.50139681 | -2.60454525 | -4.55038620 |
| H | 10.92360246 | -2.28490505 | -3.52828412 |
| H | 10.94824672 | -1.83851803 | -5.23854398 |
| H | 10.34698119 | 1.41486569 | -4.59924008 |
| H | 8.99697144 | 0.72832147 | -5.53652037 |
| H | 10.65972407 | 0.16465485 | -5.80744182 |
| H | 2.32894225 | 5.91574697 | 0.88277910 |
| H | 1.39858607 | 6.31564742 | -0.57738206 |
| H | 3.15356731 | 6.14584407 | -0.67954571 |
| H | 11.57026456 | 1.02733013 | 5.15171939 |
| H | 11.75449122 | 2.53011781 | 6.08246649 |
| H | 11.70901921 | 2.59588789 | 4.31802945 |
| H | 8.53029784 | 3.42779150 | 6.46784647 |
| H | 10.04447068 | 2.94654058 | 7.23981901 |
| H | 8.75015311 | 1.74833624 | 7.02082175 |
| H | 0.76334406 | 3.23012239 | -1.77811283 |
| H | 0.11357192 | 4.74682318 | -1.15008539 |
| H | 0.23745993 | 3.33397321 | -0.07933989 |

Table B.62 180 degree enolate complex with 4-$NMe_2$-TPPO.






180° O-Si-O enolate free energy: -3568.27807884615

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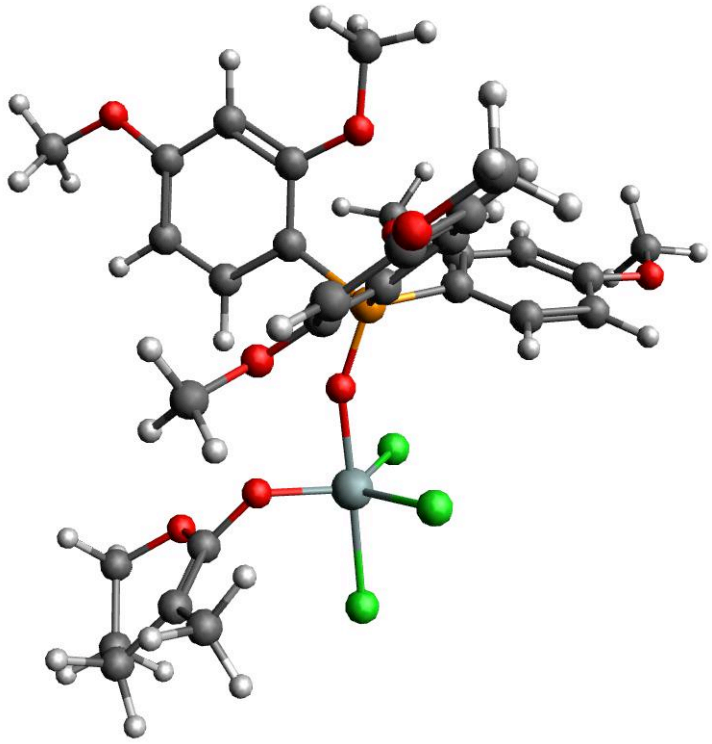
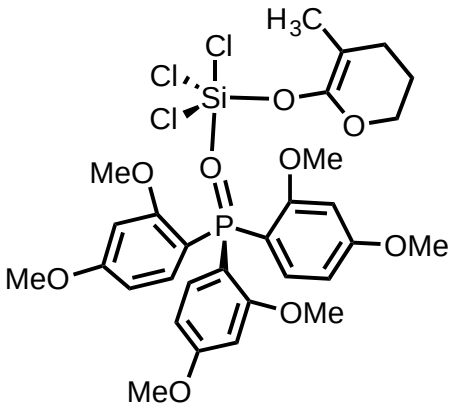
| | | | |
|---|---|---|---|
| C | -5.62431987 | -2.03879139 | -3.16962289 |
| C | -4.54158262 | -2.23335084 | -2.13016918 |
| C | -5.77108696 | -0.56299866 | -3.56228763 |
| C | -4.07704633 | -3.63919510 | -1.86199910 |
| O | -4.42841042 | 0.12595588 | -1.64713301 |
| H | -6.72306522 | -0.37763185 | -4.07722684 |
| H | -4.96276010 | -0.27154541 | -4.24540988 |
| C | -5.68419193 | 0.30011291 | -2.30920526 |
| H | -6.48939588 | 0.04056406 | -1.60454115 |
| H | -5.74436760 | 1.36928168 | -2.53199903 |
| C | -4.02028738 | -1.17187242 | -1.48037755 |
| O | -3.05061405 | -1.28889443 | -0.55585019 |
| H | -6.58885272 | -2.43048153 | -2.80214413 |
| H | -5.38562516 | -2.63703109 | -4.06275434 |
| P | 1.26764779 | 0.87527838 | 0.56861411 |
| O | -0.27638593 | 0.72725858 | 0.47308513 |
| C | 2.24620267 | -0.28351118 | -0.40048766 |
| C | 1.64132464 | 2.54520607 | -0.01098182 |
| C | 0.70791857 | 0.69693419 | 3.28853689 |
| C | 3.05183915 | 0.64268543 | 2.73565068 |
| C | 3.37870795 | 0.58011961 | 4.08463592 |
| C | 1.02165289 | 0.63380672 | 4.64033414 |
| C | 2.36774818 | 0.58205738 | 5.08039173 |
| H | 4.42460978 | 0.52437056 | 4.36228547 |
| H | 0.20814553 | 0.61947130 | 5.35523154 |
| N | 2.68259155 | 0.53667023 | 6.42355122 |

| | | | |
|---|---|---|---|
| C | 2.54535095 | -0.01092981 | -1.74789467 |
| C | 2.63495809 | -1.53143158 | 0.11891152 |
| C | 3.31143796 | -2.45828401 | -0.66096233 |
| C | 3.22013198 | -0.92885304 | -2.53870530 |
| H | 2.23109440 | 0.92792652 | -2.19358307 |
| H | 2.39076410 | -1.79211123 | 1.14395304 |
| C | 3.63035481 | -2.18231822 | -2.01596090 |
| H | 3.57558335 | -3.41009360 | -0.21617980 |
| N | 4.31156712 | -3.09485168 | -2.79351340 |
| H | 3.41042086 | -0.67461239 | -3.57433704 |
| C | 0.59543119 | 3.45237304 | -0.24268888 |
| C | 2.95945643 | 2.99378413 | -0.19178091 |
| H | -0.43207966 | 3.12813875 | -0.10991358 |
| C | 0.85357783 | 4.75744890 | -0.64458418 |
| C | 2.18036892 | 5.21589736 | -0.84087991 |
| C | 3.23152542 | 4.29446330 | -0.59569174 |
| H | 4.26538787 | 4.59085572 | -0.72653902 |
| H | 3.79460863 | 2.31722292 | -0.02780887 |
| H | 0.01250143 | 5.41946373 | -0.81275190 |
| N | 2.44147664 | 6.50429411 | -1.26130149 |
| C | 3.81337829 | 6.97924478 | -1.34344932 |
| H | 3.81512589 | 8.00839554 | -1.70673950 |
| H | 4.40291196 | 6.37707184 | -2.04721962 |
| H | 4.32043205 | 6.96025910 | -0.36613685 |
| C | 4.55962506 | -4.43703663 | -2.28484667 |
| H | 5.13225509 | -4.99776985 | -3.02560356 |
| H | 3.62742853 | -4.98535221 | -2.07974310 |
| H | 5.15111916 | -4.40440624 | -1.36205820 |
| C | 4.06473103 | 0.36353480 | 6.84188113 |
| H | 4.48864582 | -0.59363467 | 6.49966579 |
| H | 4.11260048 | 0.38691371 | 7.93190801 |
| H | 4.69933102 | 1.17495361 | 6.46311628 |
| C | 1.71495165 | 0.70221951 | 2.31010126 |
| H | 3.85968318 | 0.62999261 | 2.00762338 |
| H | -0.33445853 | 0.73270057 | 2.98772513 |
| Si | -1.72951269 | -0.30045809 | -0.08779154 |
| Cl | -2.88727026 | 1.05022975 | 1.06598809 |
| Cl | -0.88941966 | -1.95622974 | 0.95149290 |
| Cl | -1.13191955 | 0.13639363 | -2.09225207 |
| H | -4.91442346 | -4.28174330 | -1.54525074 |
| H | -3.31395553 | -3.66877296 | -1.08020771 |
| H | -3.65463681 | -4.10084823 | -2.76872443 |
| C | 1.62253432 | 0.40787648 | 7.41326282 |
| C | 1.35044127 | 7.45708099 | -1.40207279 |
| C | 4.47227229 | -2.85197088 | -4.22063529 |
| H | 5.06481777 | -3.65929742 | -4.65461296 |

| | | | |
|---|---|---|---|
| H | 5.00783163 | -1.91241072 | -4.40191119 |
| H | 3.50745069 | -2.80770460 | -4.74930843 |
| H | 0.92754945 | 1.25573977 | 7.36410049 |
| H | 2.06533429 | 0.39789749 | 8.41079274 |
| H | 1.04314691 | -0.51897997 | 7.28403645 |
| H | 0.60871736 | 7.10783352 | -2.13185169 |
| H | 1.74966349 | 8.40667956 | -1.76230862 |
| H | 0.83320294 | 7.64131631 | -0.44801492 |

Table B.63 90 degree enolate complex with 2,4-diOMe-TPPO.






90° O-Si-O enolate free energy: -3853.51464607118

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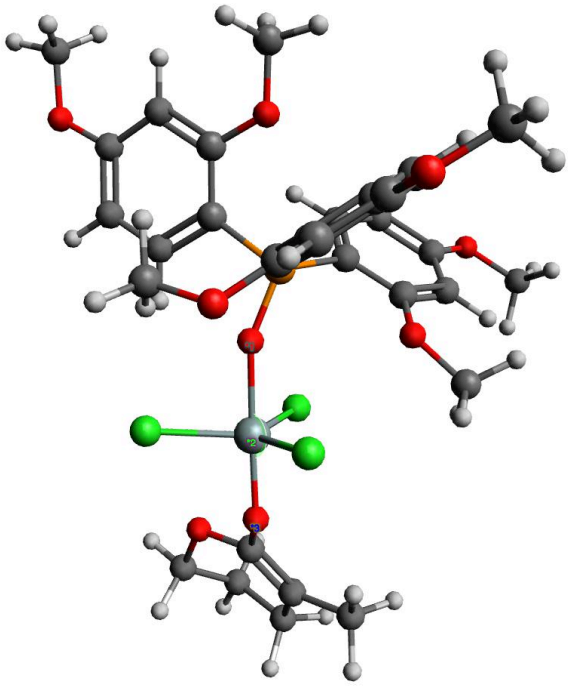
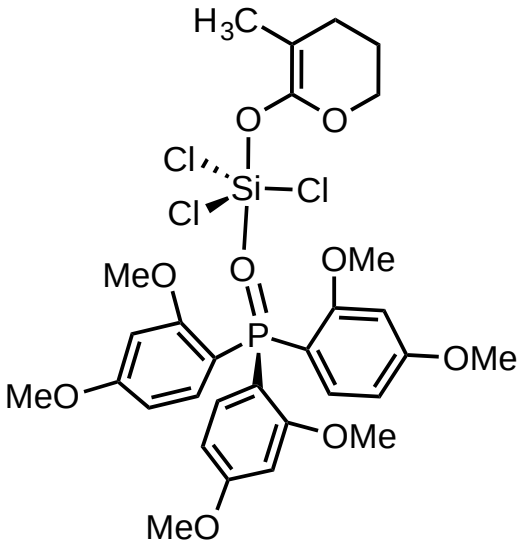
| | | | |
|---|---|---|---|
| C | 0.81131021 | -4.01541290 | 0.89580552 |
| C | 2.14163608 | -3.30951863 | 1.05193497 |
| C | 0.36536201 | -4.05435108 | -0.57162618 |
| C | 2.87718528 | -3.50597236 | 2.34904786 |
| O | 2.04913161 | -2.39399502 | -1.17948641 |
| H | -0.70329108 | -4.28885255 | -0.65996649 |
| H | 0.92178687 | -4.82892715 | -1.11350354 |
| C | 0.65153910 | -2.70558143 | -1.22080594 |
| H | 0.10102567 | -1.90374544 | -0.70332178 |
| H | 0.38678328 | -2.68576362 | -2.28162797 |
| C | 2.66692689 | -2.62357852 | 0.02095324 |

| | | | |
|---|---|---|---|
| O | 3.86259725 | -1.98905810 | 0.04635685 |
| H | 3.77570584 | -2.88764152 | 2.40894087 |
| H | 0.03975405 | -3.53159756 | 1.51831816 |
| H | 0.90247837 | -5.04201607 | 1.28098976 |
| H | 2.23314354 | -3.26183468 | 3.20853190 |
| P | 6.68692555 | 0.56713109 | -0.05990473 |
| O | 5.78825660 | -0.67657234 | -0.19595737 |
| C | 8.18432393 | 0.37851409 | -1.06476449 |
| C | 5.63244362 | 1.95783749 | -0.53174380 |
| C | 6.26256147 | 0.71097792 | 2.71376237 |
| C | 8.48455371 | 1.31501670 | 1.98738301 |
| C | 8.86993085 | 1.58117437 | 3.30298514 |
| C | 6.63499385 | 0.96260208 | 4.03350716 |
| C | 7.93772417 | 1.38867090 | 4.32949171 |
| H | 9.87767415 | 1.92371004 | 3.50505407 |
| H | 5.93948840 | 0.83854665 | 4.85428531 |
| O | 8.19173278 | 1.59669439 | 5.65055450 |
| C | 8.30191937 | 0.84566232 | -2.39195831 |
| C | 9.20624070 | -0.45661561 | -0.57066142 |
| C | 10.32929517 | -0.77267327 | -1.31842429 |
| C | 9.43590513 | 0.54015044 | -3.15855882 |
| O | 7.27484285 | 1.58449349 | -2.88336408 |
| H | 9.10314059 | -0.89321008 | 0.41721218 |
| C | 10.44841117 | -0.26200966 | -2.61856468 |
| H | 11.10305024 | -1.42554857 | -0.92898575 |
| O | 11.57983010 | -0.60323237 | -3.29129925 |
| H | 9.51503930 | 0.91218005 | -4.17025001 |
| C | 4.29364390 | 1.70919735 | -0.83465644 |
| C | 6.09438316 | 3.29312364 | -0.53089587 |
| H | 3.93789387 | 0.68391972 | -0.81941546 |
| C | 3.40909767 | 2.74685473 | -1.14310361 |
| C | 3.88325136 | 4.06266998 | -1.13812767 |
| C | 5.22690682 | 4.33926930 | -0.83016660 |
| H | 5.55062938 | 5.37294125 | -0.84040776 |
| O | 7.41255656 | 3.46465817 | -0.23131655 |
| H | 2.37642685 | 2.51474695 | -1.37368559 |
| O | 3.12322466 | 5.15943200 | -1.41801956 |
| C | 7.20587519 | 0.85670638 | 1.65876583 |
| H | 9.20914563 | 1.47937553 | 1.19765252 |
| O | 5.01384433 | 0.34471300 | 2.35081230 |
| Si | 5.41094734 | -2.45589111 | -0.43771440 |
| Cl | 4.90525041 | -4.57644004 | -0.71400189 |
| Cl | 6.86717716 | -2.91335707 | 1.05440145 |
| Cl | 6.07100463 | -2.26022193 | -2.44877644 |
| H | 3.18934076 | -4.55389060 | 2.47067593 |
| C | 1.74954756 | 4.97116306 | -1.74443334 |

| | | | |
|---|---|---|---|
| C | 4.01627454 | 0.13803481 | 3.34619728 |
| C | 9.49575838 | 2.01680908 | 6.03943084 |
| C | 11.74445584 | -0.17327683 | -4.63824663 |
| C | 7.22864972 | 1.89409326 | -4.27173051 |
| C | 7.94493260 | 4.78265471 | -0.17507740 |
| H | 8.99761060 | 4.66450998 | 0.08679152 |
| H | 7.43996002 | 5.38028706 | 0.59414045 |
| H | 7.86351262 | 5.28413238 | -1.14771319 |
| H | 9.46570038 | 2.09883509 | 7.12700195 |
| H | 9.74328001 | 2.99347104 | 5.60481467 |
| H | 10.25314463 | 1.27865606 | 5.74761278 |
| H | 3.12914395 | -0.18428621 | 2.80080822 |
| H | 3.80640881 | 1.06718817 | 3.89145177 |
| H | 4.31935322 | -0.64794768 | 4.04792419 |
| H | 1.35271768 | 5.96990119 | -1.93343058 |
| H | 1.20357870 | 4.51068557 | -0.91150617 |
| H | 1.63695293 | 4.35445269 | -2.64484268 |
| H | 12.70785656 | -0.57296515 | -4.95824758 |
| H | 11.76283759 | 0.92213887 | -4.70633893 |
| H | 10.95062702 | -0.57312898 | -5.28164238 |
| H | 6.27311145 | 2.39708156 | -4.42665254 |
| H | 7.26485239 | 0.98044393 | -4.87679559 |
| H | 8.04542445 | 2.56908564 | -4.55873559 |

Table B.64 180 degree enolate complex with 2,4-diOMe-TPPO.






180° O-Si-O enolate free energy: -3853.50032277513

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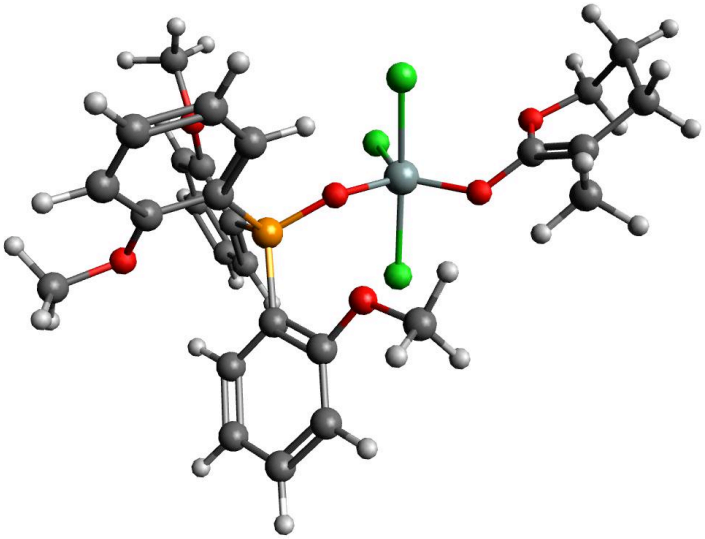
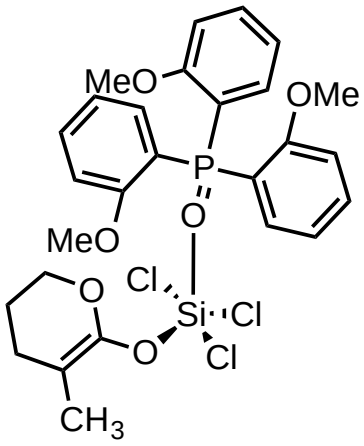
| | | | |
|---|---|---|---|
| C | -5.19949670 | -2.86301118 | -2.90177122 |
| C | -4.47151370 | -2.58771736 | -1.60400667 |
| C | -5.05356159 | -1.69535416 | -3.88675676 |
| C | -4.26205112 | -3.74290180 | -0.66313619 |
| O | -4.21435494 | -0.24482752 | -2.11331155 |
| H | -5.79809990 | -1.75200424 | -4.69166965 |
| H | -4.05977656 | -1.71591986 | -4.35220918 |
| C | -5.20987959 | -0.37997972 | -3.13309210 |
| H | -6.20218247 | -0.32104026 | -2.66005614 |
| H | -5.07673017 | 0.49190092 | -3.77979861 |
| C | -4.02020291 | -1.34802142 | -1.32313886 |
| O | -3.35002496 | -1.05063670 | -0.19461434 |
| H | -6.26686857 | -3.06914909 | -2.71196938 |
| H | -4.79906175 | -3.78278769 | -3.35593363 |
| P | 1.27799568 | 0.84771411 | 0.62126775 |
| O | -0.25179441 | 0.69863534 | 0.47008930 |
| C | 2.22958019 | -0.30144230 | -0.41228113 |
| C | 1.65216445 | 2.52155480 | 0.00932938 |
| C | 1.03300371 | 1.01267283 | 3.49827867 |
| C | 2.99085653 | -0.06063073 | 2.58251655 |
| C | 3.44260677 | -0.41024603 | 3.85083259 |
| C | 1.47416927 | 0.64801209 | 4.77323771 |
| C | 2.65918001 | -0.06564969 | 4.96185026 |
| H | 4.37283596 | -0.95676901 | 3.95217109 |
| H | 0.87297523 | 0.93261097 | 5.62992776 |
| O | 2.97401022 | -0.36420347 | 6.25266195 |
| C | 3.03312900 | 0.16350842 | -1.46688050 |
| C | 2.08164106 | -1.69863495 | -0.26007845 |
| C | 2.72173019 | -2.58973899 | -1.13095413 |
| C | 3.67855912 | -0.70407464 | -2.33574003 |
| H | 3.14305802 | 1.23092100 | -1.62121097 |
| O | 1.29934308 | -2.09919263 | 0.76554564 |
| C | 3.51625625 | -2.08747269 | -2.16965515 |
| H | 2.58501539 | -3.65459674 | -1.00496582 |
| O | 4.17122704 | -2.87235460 | -3.06586113 |
| H | 4.29003452 | -0.33705299 | -3.15322465 |
| C | 0.66120544 | 3.19915874 | -0.72219004 |
| C | 2.88326532 | 3.17453952 | 0.22119380 |
| H | -0.29335324 | 2.71042676 | -0.88646488 |
| C | 0.86608498 | 4.47892684 | -1.21750872 |
| C | 2.09117038 | 5.11991632 | -0.98422337 |
| C | 3.10484032 | 4.47165668 | -0.26305249 |
| H | 4.05450066 | 4.95710617 | -0.08752708 |
| O | 3.83347823 | 2.46766756 | 0.89484602 |

| | | | |
|---|---|---|---|
| H | 0.09397997 | 4.99671837 | -1.77667721 |
| O | 2.21348355 | 6.37304299 | -1.49772644 |
| C | 3.42594304 | 7.09197698 | -1.30210927 |
| H | 3.28039928 | 8.05370371 | -1.79607166 |
| H | 4.27591250 | 6.57104550 | -1.76156702 |
| H | 3.62357979 | 7.25595328 | -0.23495107 |
| C | 4.01682173 | -4.28657315 | -2.99449080 |
| H | 4.61207046 | -4.68842111 | -3.81572781 |
| H | 2.96725774 | -4.57778482 | -3.12585674 |
| H | 4.39541047 | -4.67967806 | -2.04233498 |
| C | 4.16628170 | -1.09503229 | 6.51532489 |
| H | 4.14425296 | -2.07980255 | 6.03148639 |
| H | 4.20023145 | -1.22291803 | 7.59844850 |
| H | 5.05435219 | -0.54097261 | 6.18464995 |
| C | 1.78905634 | 0.63072554 | 2.35436810 |
| H | 3.59540927 | -0.35323156 | 1.73045464 |
| O | -0.15573257 | 1.67322453 | 3.49489113 |
| Si | -1.88456119 | -0.20042627 | 0.09224630 |
| Cl | -1.70256003 | -1.15345224 | 1.96634410 |
| Cl | -0.94730425 | -0.90990414 | -1.68934931 |
| Cl | -2.76127743 | 1.72505359 | 0.09876973 |
| H | -5.21893555 | -4.22372746 | -0.40467966 |
| H | -3.78409461 | -3.42225970 | 0.26602122 |
| H | -3.63412721 | -4.52463950 | -1.12071083 |
| C | 5.07498741 | 3.08144929 | 1.22200940 |
| C | 0.91008873 | -3.46747567 | 0.87597134 |
| C | -0.29968859 | 2.92139689 | 2.80335382 |
| H | -1.04903492 | 3.48464947 | 3.36487164 |
| H | -0.66022799 | 2.76401899 | 1.78643466 |
| H | 0.64688808 | 3.47413731 | 2.80017186 |
| H | 5.64125442 | 3.34090011 | 0.31851346 |
| H | 5.62712833 | 2.33489789 | 1.79472543 |
| H | 4.92389855 | 3.97602757 | 1.83881763 |
| H | 0.21590391 | -3.50171351 | 1.71504214 |
| H | 1.77692629 | -4.10807128 | 1.08251891 |
| H | 0.39969173 | -3.79581663 | -0.03663809 |

Table B.65 120 degree enolate complex with 2-OMe-TPPO.






120° O-Si-O enolate free energy: -3509.92272719650

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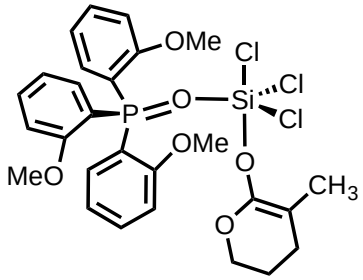
| | | | |
|---|---|---|---|
| C | -0.01130804 | 0.88424216 | -1.36312651 |
| C | 1.47549967 | 0.60585626 | -1.30971027 |
| C | -0.53222560 | 1.40562586 | -0.01716201 |
| C | 2.19390026 | 0.39113144 | -2.61267615 |
| O | 1.51507272 | 0.68463806 | 1.09936925 |
| H | -1.62673230 | 1.34399025 | 0.03737323 |
| H | -0.25109742 | 2.45807586 | 0.11354442 |
| C | 0.08548129 | 0.58894200 | 1.11110356 |
| H | -0.19061857 | -0.47231034 | 1.01813218 |
| H | -0.21368731 | 0.94536426 | 2.09990516 |
| C | 2.10897256 | 0.57237834 | -0.12332141 |
| O | 3.43720465 | 0.33243727 | 0.01204628 |
| H | 3.23063680 | 0.08702449 | -2.45068074 |
| H | -0.56413666 | -0.02313273 | -1.65930328 |
| H | -0.21478197 | 1.62583361 | -2.15044250 |
| H | 1.70143038 | -0.39388696 | -3.20744767 |
| P | 7.62413687 | 1.75450066 | 0.40143962 |
| Cl | 4.42853997 | 1.27364639 | 3.06252519 |
| C | 8.41113448 | 0.40014567 | -0.52386471 |
| C | 8.09338191 | 3.27916460 | -0.46173024 |
| C | 8.34834092 | 0.45886743 | 2.77578734 |
| C | 8.09871016 | 2.86962317 | 2.93359063 |
| C | 8.37230979 | 2.79628317 | 4.30491519 |
| C | 8.61133016 | 0.38863079 | 4.14314048 |
| C | 8.63227965 | 1.56094819 | 4.89843185 |
| H | 8.36462706 | 3.69402416 | 4.91194967 |

| | | | |
|---|---|---|---|
| H | 8.76875016 | -0.57659741 | 4.61443340 |
| H | 8.82980823 | 1.51778089 | 5.96635173 |
| C | 7.86566007 | -0.00777318 | -1.76570677 |
| C | 9.61684690 | -0.17139810 | -0.09518743 |
| C | 10.25083914 | -1.16677179 | -0.83901583 |
| C | 8.49650624 | -1.01775182 | -2.50513114 |
| O | 6.75387216 | 0.64136545 | -2.17874474 |
| H | 10.07295782 | 0.16972694 | 0.82657686 |
| C | 9.67790339 | -1.59347797 | -2.03703081 |
| H | 11.17908008 | -1.60354060 | -0.48293627 |
| H | 10.15324817 | -2.37552272 | -2.62344695 |
| H | 8.07118186 | -1.35241280 | -3.44382331 |
| C | 7.10481289 | 4.04343378 | -1.09025909 |
| C | 9.44604714 | 3.66260748 | -0.56536328 |
| H | 6.06437230 | 3.75434814 | -0.97947200 |
| C | 7.45489164 | 5.17189467 | -1.83626941 |
| C | 8.79740317 | 5.53156961 | -1.95314615 |
| C | 9.79770161 | 4.78638930 | -1.31959760 |
| H | 10.83499568 | 5.08699841 | -1.41463442 |
| O | 10.33833907 | 2.88294489 | 0.11059551 |
| H | 6.68081876 | 5.75798755 | -2.32310685 |
| H | 9.08025857 | 6.40138512 | -2.54093178 |
| C | 8.12101812 | 1.69276242 | 2.14454872 |
| O | 7.79039059 | 4.02442018 | 2.29424169 |
| H | 8.27018357 | -0.45865190 | 2.20493776 |
| Si | 4.58744096 | 1.09714134 | 0.97216489 |
| O | 6.05971433 | 1.75928829 | 0.31083112 |
| Cl | 3.72131863 | 3.12551594 | 0.59840993 |
| Cl | 5.60958339 | -0.90492339 | 1.09888105 |
| H | 2.19185883 | 1.30248862 | -3.23158249 |
| C | 7.47042882 | 5.19230544 | 3.04893696 |
| C | 11.73049316 | 3.15900713 | -0.00802652 |
| C | 6.15241991 | 0.28431463 | -3.42112204 |
| H | 8.35625314 | 5.58750457 | 3.56168519 |
| H | 6.67553674 | 4.98164045 | 3.77304818 |
| H | 7.11619812 | 5.91848940 | 2.31597648 |
| H | 5.30009890 | 0.95429659 | -3.53311831 |
| H | 5.80303151 | -0.75434933 | -3.40185291 |
| H | 6.85331230 | 0.43349863 | -4.25180795 |
| H | 12.05746588 | 3.09051182 | -1.05264133 |
| H | 12.23470461 | 2.39352461 | 0.58339972 |
| H | 11.97317200 | 4.14959468 | 0.39567759 |

Table B.66 90 degree enolate complex (swapped) with 2-OMe-TPPO.



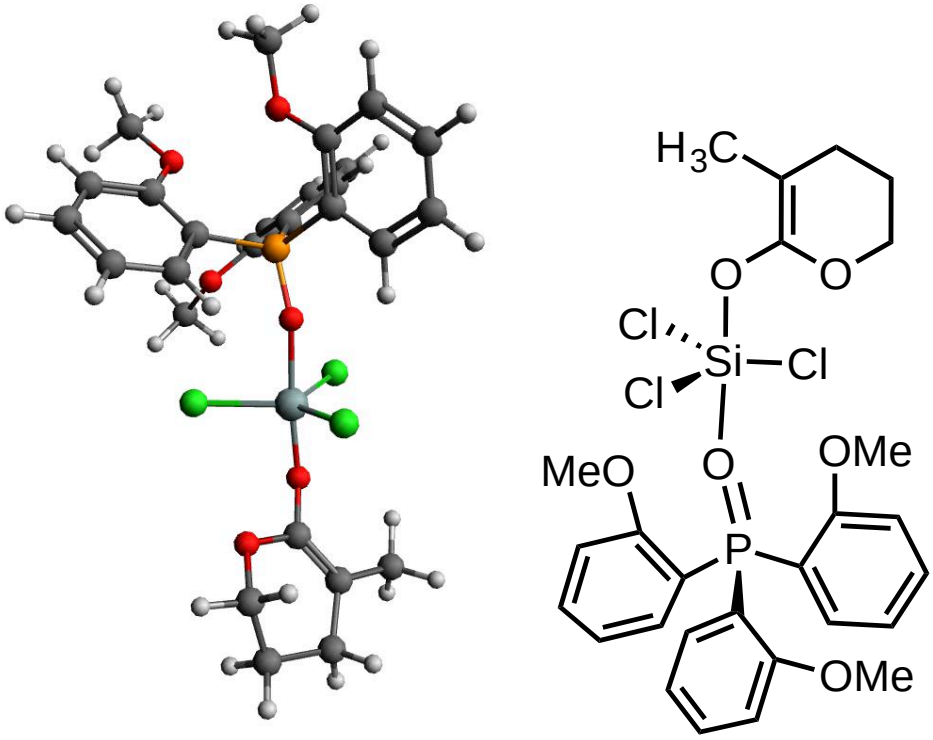

90° O-Si-O enolate free energy: -3509.92113170522

68

| | | | |
|---|---|---|---|
| C | 0.16175426 | 1.46066338 | -0.00350786 |
| C | 1.32792517 | 0.49689068 | -0.04349189 |
| C | 0.61008516 | 2.90012229 | -0.28503560 |
| C | 1.00735965 | -0.97238888 | -0.09525100 |
| O | 2.95235661 | 2.28331887 | -0.00592989 |
| H | -0.14934623 | 3.62716931 | 0.03048202 |
| H | 0.77847263 | 3.03948864 | -1.36035977 |
| C | 1.91802813 | 3.16554609 | 0.44881638 |
| H | 1.78796802 | 3.02336310 | 1.53289047 |
| H | 2.29938551 | 4.17574235 | 0.27147561 |
| C | 2.59560675 | 0.94907525 | -0.09130784 |
| O | 3.67865922 | 0.16138706 | -0.17150007 |
| H | 1.90917076 | -1.58737621 | -0.04765606 |
| H | -0.35371656 | 1.40406763 | 0.97013510 |
| H | -0.58566007 | 1.15303802 | -0.75056131 |
| H | 0.35050890 | -1.26140621 | 0.73996552 |
| P | 7.22232790 | 1.50602475 | -0.10817105 |
| O | 5.92394118 | 0.95182602 | -0.77290685 |
| C | 8.69416303 | 0.67261952 | -0.73885365 |
| C | 7.15499484 | 3.29992809 | -0.40019088 |
| C | 5.93341787 | 0.47840067 | 2.14658408 |
| C | 8.00329540 | 1.66218530 | 2.60395973 |
| C | 7.83585871 | 1.42636528 | 3.97199539 |
| C | 5.76724708 | 0.24215819 | 3.51387212 |
| C | 6.71739368 | 0.71417176 | 4.41725360 |
| H | 8.56282500 | 1.79156954 | 4.68853117 |
| H | 4.89549358 | -0.30460966 | 3.85986484 |
| H | 6.59526551 | 0.53567515 | 5.48266171 |
| C | 9.11801233 | 0.89194036 | -2.06932325 |
| C | 9.34266431 | -0.29293396 | 0.04047849 |
| C | 10.40472581 | -1.03395086 | -0.47820539 |
| C | 10.17852917 | 0.14352842 | -2.59061343 |
| O | 8.45506172 | 1.84936508 | -2.75964527 |
| H | 9.00504823 | -0.47979673 | 1.05486634 |

| | | | |
|---|---|---|---|
| C | 10.81337676 | -0.81170784 | -1.79407742 |
| H | 10.89202936 | -1.78704149 | 0.13356663 |
| H | 11.62997918 | -1.39236414 | -2.21566426 |
| H | 10.50002897 | 0.29257232 | -3.61506447 |
| C | 5.86701586 | 3.85396250 | -0.45683563 |
| C | 8.27944228 | 4.14080847 | -0.56845378 |
| H | 4.99939069 | 3.20921899 | -0.34706480 |
| C | 5.68478536 | 5.22023145 | -0.67574416 |
| C | 6.79767077 | 6.04276425 | -0.84203321 |
| C | 8.08803310 | 5.51130010 | -0.79029472 |
| H | 8.94051807 | 6.16681389 | -0.92493361 |
| O | 9.50877111 | 3.56559066 | -0.51190942 |
| H | 4.68026929 | 5.62938276 | -0.72675606 |
| H | 6.67105995 | 7.10811297 | -1.01808603 |
| C | 7.05262597 | 1.17873686 | 1.67662750 |
| O | 9.04909773 | 2.34573480 | 2.06782590 |
| H | 5.17738206 | 0.13591282 | 1.44851831 |
| Si | 4.81010033 | -0.20666126 | -1.45238284 |
| Cl | 4.95679920 | -2.17706557 | -0.65989310 |
| Cl | 3.48140677 | 0.45862132 | -2.97418775 |
| Cl | 6.31559145 | -0.73195988 | -3.02194714 |
| H | 0.47212032 | -1.22982575 | -1.02206750 |
| C | 10.05429737 | 2.87174027 | 2.92698118 |
| C | 10.64993842 | 4.31695630 | -0.90389484 |
| C | 8.52944399 | 1.86091540 | -4.18702788 |
| H | 10.57106383 | 2.06900681 | 3.46786703 |
| H | 9.62969834 | 3.58795031 | 3.64142258 |
| H | 10.75991844 | 3.38289930 | 2.27118320 |
| H | 7.79449190 | 2.59976760 | -4.50850169 |
| H | 8.26160874 | 0.87933240 | -4.59038328 |
| H | 9.52808210 | 2.16237920 | -4.52767694 |
| H | 10.53191431 | 4.71923047 | -1.91782078 |
| H | 11.48289204 | 3.61182890 | -0.88540447 |
| H | 10.85114265 | 5.13832652 | -0.20339807 |

Table B.67 180 degree enolate complex with 2-OMe-TPPO.




180° O-Si-O enolate free energy: -3509.92652111562

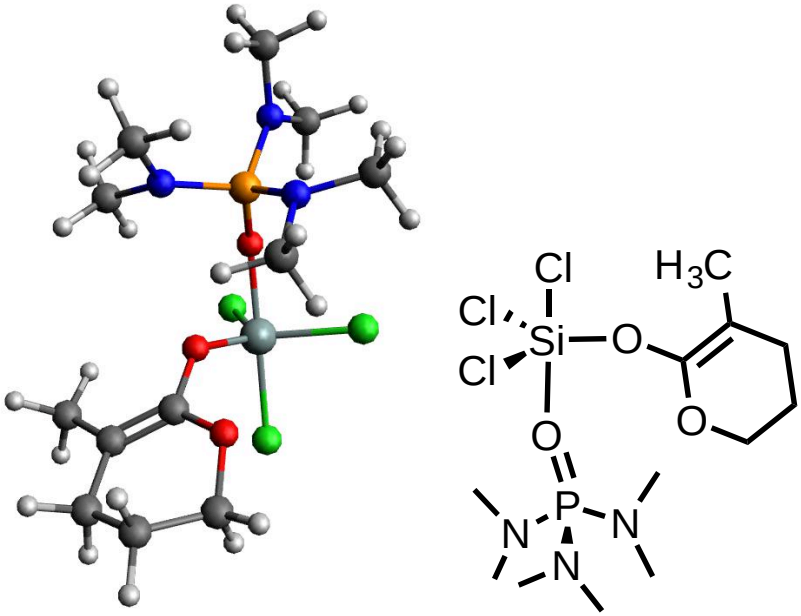
68

| | | | |
|---|---|---|---|
| C | -0.73701318 | 0.62428358 | -1.36550882 |
| C | 0.70117643 | 0.15320706 | -1.40280724 |
| C | -0.84867336 | 2.14470213 | -1.54271231 |
| C | 0.94041084 | -1.33125687 | -1.45578359 |
| O | 1.55532216 | 2.40412766 | -1.28748541 |
| H | -1.81775179 | 2.51986697 | -1.18819936 |
| H | -0.76142914 | 2.41195047 | -2.60411550 |
| C | 0.28379903 | 2.82376394 | -0.78134298 |
| H | 0.23725525 | 2.58033175 | 0.29088623 |
| H | 0.27308075 | 3.91126721 | -0.89843707 |
| C | 1.71229913 | 1.04528132 | -1.39456359 |
| Cl | 3.45750548 | 1.24481202 | 1.20892928 |
| H | 2.00659932 | -1.57047586 | -1.43667163 |
| H | -1.20170097 | 0.31900692 | -0.41279743 |
| H | -1.31569129 | 0.11472375 | -2.15188410 |
| H | 0.46088292 | -1.84021978 | -0.60444336 |
| P | 7.50217128 | 1.80031340 | 0.54459499 |
| O | 6.00261126 | 1.51777557 | 0.30783067 |
| C | 8.58138839 | 0.68977065 | -0.40050240 |
| C | 7.79802369 | 3.58059514 | 0.28369509 |

| | | | |
|---|---|---|---|
| C | 6.71321198 | 0.89500594 | 3.05358088 |
| C | 8.95804671 | 1.81117170 | 2.98526353 |
| C | 9.08898467 | 1.58692066 | 4.36042554 |
| C | 6.84430341 | 0.66371937 | 4.42524909 |
| C | 8.02936170 | 1.01358679 | 5.07075064 |
| H | 10.00252564 | 1.85482777 | 4.87937814 |
| H | 6.02193727 | 0.22070198 | 4.97890484 |
| H | 8.13975351 | 0.84496598 | 6.13905959 |
| C | 8.57545709 | 0.74362413 | -1.81163536 |
| C | 9.32858073 | -0.30238875 | 0.24220907 |
| C | 10.07659976 | -1.22537341 | -0.49192617 |
| C | 9.31714451 | -0.18466899 | -2.55056368 |
| O | 7.82443708 | 1.72808260 | -2.35519601 |
| H | 9.31737311 | -0.36690056 | 1.32490373 |
| C | 10.06523930 | -1.15942938 | -1.88523960 |
| H | 10.64544549 | -1.99508908 | 0.02117454 |
| H | 10.63387869 | -1.87885929 | -2.46912148 |
| H | 9.30640648 | -0.15849746 | -3.63435799 |
| C | 6.77120182 | 4.42004475 | 0.73981683 |
| C | 8.94853638 | 4.15871240 | -0.29626955 |
| H | 5.87657215 | 3.97877667 | 1.16858529 |
| C | 6.86583911 | 5.80690422 | 0.63036749 |
| C | 8.00198376 | 6.36635272 | 0.04786046 |
| C | 9.03842497 | 5.55296743 | -0.41494285 |
| H | 9.91274136 | 6.00925180 | -0.86485679 |
| O | 9.92844045 | 3.31493509 | -0.71512479 |
| H | 6.05325687 | 6.43530184 | 0.98166263 |
| H | 8.08865529 | 7.44476367 | -0.05712405 |
| C | 7.76060028 | 1.46605493 | 2.32024183 |
| O | 9.93480374 | 2.34718885 | 2.20358924 |
| H | 5.78703010 | 0.65054105 | 2.54463791 |
| Si | 4.42146605 | 1.15845551 | -0.69219470 |
| Cl | 5.37967561 | -0.60493962 | -1.37241389 |
| O | 3.00384047 | 0.69568824 | -1.54798136 |
| Cl | 4.74260254 | 2.94840563 | -1.75830736 |
| H | 0.50989157 | -1.77537741 | -2.36755208 |
| C | 11.16219341 | 2.75020924 | 2.80044932 |
| C | 11.04751674 | 3.83898256 | -1.41774775 |
| C | 7.50939910 | 1.68598593 | -3.74731385 |
| H | 11.68180696 | 1.89517382 | 3.25102657 |
| H | 10.99584376 | 3.52621367 | 3.55779680 |
| H | 11.76341090 | 3.15486227 | 1.98521825 |
| H | 6.79768772 | 2.49553821 | -3.90604461 |
| H | 7.04046398 | 0.72964512 | -4.00462161 |
| H | 8.40537075 | 1.84927301 | -4.35934664 |
| H | 10.73376542 | 4.38826456 | -2.31439047 |

| | | | |
|---|---|---|---|
| H | 11.64048745 | 2.97065627 | -1.70993742 |
| H | 11.65158800 | 4.49543058 | -0.77694363 |

Table B.68 90 degree enolate complex with HMPA.




90° O-Si-O enolate free energy: -2875.13789156895

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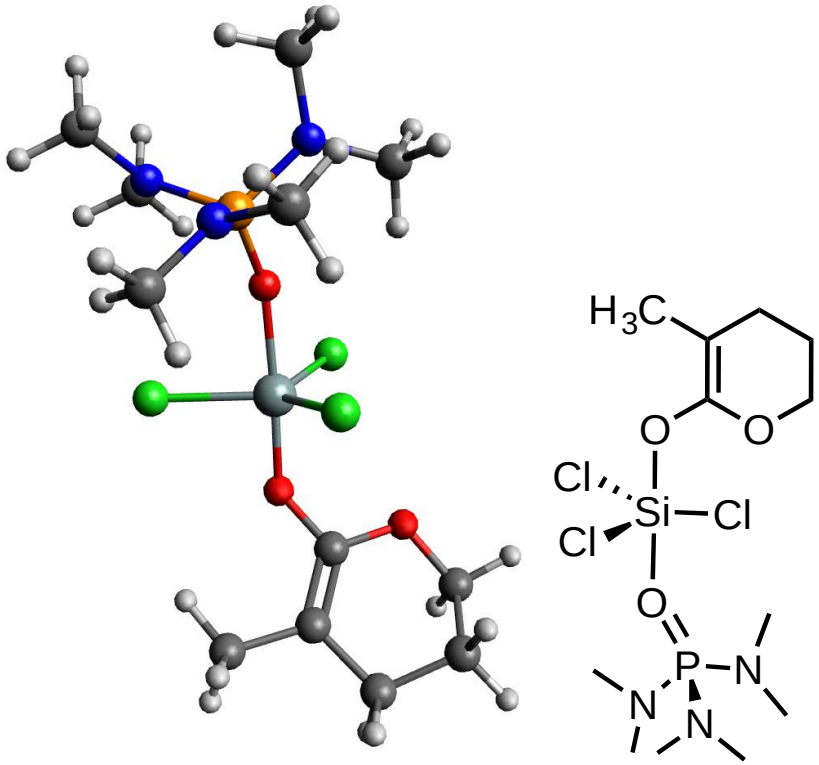
| | | | |
|---|---|---|---|
| C | 5.54728459 | -6.56799923 | -0.93124130 |
| C | 5.19816891 | -5.30827523 | -0.16766199 |
| C | 5.87029638 | -6.28520266 | -2.40551567 |
| C | 5.02990605 | -5.43416601 | 1.32166345 |
| O | 5.06716037 | -3.99818833 | -2.18820501 |
| H | 5.78000771 | -7.19715853 | -3.00897924 |
| H | 6.90280943 | -5.92594731 | -2.50964342 |
| C | 4.92439066 | -5.21486535 | -2.93865106 |
| H | 3.87712415 | -5.53900574 | -2.86989801 |
| H | 5.14442865 | -4.93916803 | -3.97347080 |
| C | 4.99547614 | -4.15708720 | -0.82958135 |
| O | 4.77715356 | -2.95494083 | -0.23189330 |
| H | 5.96320924 | -5.76437969 | 1.80319253 |
| H | 4.70775166 | -7.27856876 | -0.85883986 |
| H | 6.40101776 | -7.06974571 | -0.45103812 |
| H | 4.26642159 | -6.18855425 | 1.56288898 |
| P | 5.87811347 | 0.05943861 | 0.06938255 |
| O | 4.52999239 | -0.62131427 | 0.34870336 |
| N | 6.37282476 | 0.25881636 | -1.50860650 |
| N | 5.71214403 | 1.57716673 | 0.74128962 |
| N | 7.09732177 | -0.83721305 | 0.75881917 |

| | | | |
|---|---|---|---|
| Si | 3.37551732 | -2.00295629 | -0.21401755 |
| Cl | 2.01147263 | -3.60016695 | -0.81482483 |
| Cl | 2.38035207 | -1.67148129 | 1.62132662 |
| Cl | 2.85021924 | -0.76771094 | -1.86160145 |
| H | 4.72350149 | -4.49340745 | 1.78479994 |
| C | 8.51858408 | -0.65946696 | 0.46624319 |
| C | 6.83597035 | -1.53848342 | 2.02171523 |
| C | 4.41459045 | 2.17104316 | 1.07586333 |
| C | 6.84580260 | 2.48861980 | 0.86269138 |
| C | 5.86485220 | 1.38071306 | -2.30833190 |
| C | 6.72607681 | -0.91128631 | -2.33264290 |
| H | 5.76922471 | -1.72417730 | 2.13989773 |
| H | 7.20073621 | -0.95657240 | 2.88130997 |
| H | 7.35114544 | -2.50547007 | 2.00493856 |
| H | 8.65597331 | -0.12716144 | -0.47604914 |
| H | 8.99766295 | -1.64350821 | 0.38021873 |
| H | 9.02565620 | -0.10266018 | 1.26909163 |
| H | 7.05878457 | -1.73817018 | -1.70567750 |
| H | 7.53617254 | -0.63053600 | -3.01789542 |
| H | 5.86291480 | -1.25412963 | -2.91448046 |
| H | 7.78149704 | 1.99808909 | 0.58750969 |
| H | 6.93482727 | 2.84245726 | 1.89855455 |
| H | 6.72144776 | 3.36646880 | 0.21065117 |
| H | 5.59357679 | 2.22001072 | -1.66633415 |
| H | 4.98107367 | 1.08394074 | -2.88615717 |
| H | 6.65064335 | 1.70985938 | -2.99944215 |
| H | 3.63168793 | 1.41597751 | 1.02409707 |
| H | 4.17007709 | 2.99373568 | 0.38721787 |
| H | 4.45120583 | 2.57254829 | 2.09645394 |

Table B.69 180 degree enolate complex with HMPA.




180° O-Si-O enolate free energy: -2875.13042685048

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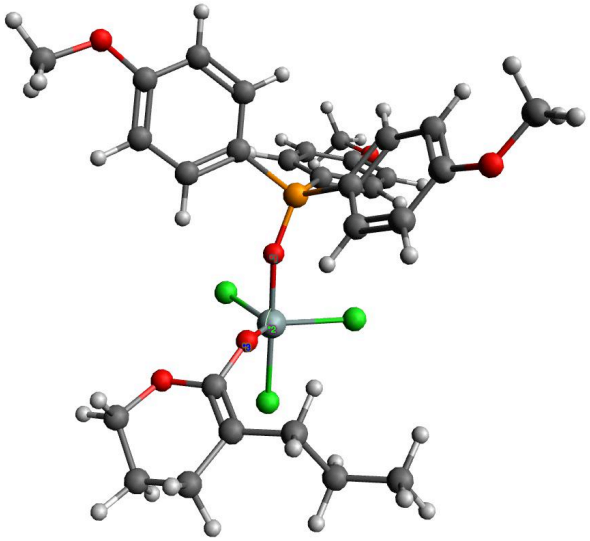
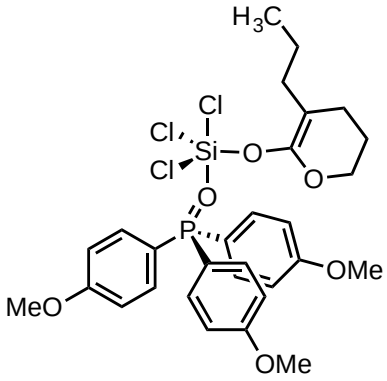
| | | | |
|---|---|---|---|
| C | -5.05219076 | -3.20103322 | -2.07264982 |
| C | -4.14229163 | -2.81133373 | -0.92719751 |
| C | -5.15708048 | -2.08270844 | -3.11798845 |
| C | -3.71816937 | -3.89937722 | 0.02195615 |
| O | -4.11947884 | -0.49134076 | -1.58776878 |
| H | -6.02507661 | -2.22928616 | -3.77357168 |
| H | -4.26135724 | -2.07213160 | -3.75217014 |
| C | -5.26720960 | -0.73878202 | -2.40794574 |
| H | -6.16337398 | -0.71045983 | -1.76942443 |
| H | -5.30664502 | 0.10205493 | -3.10598217 |
| C | -3.73175467 | -1.53513831 | -0.78854275 |
| O | -2.90860389 | -1.13073345 | 0.19913555 |
| H | -6.05453684 | -3.46358985 | -1.69372182 |
| H | -4.66742164 | -4.11750795 | -2.54566391 |
| P | 1.71229860 | 0.81422560 | 0.32311901 |
| O | 0.18500022 | 0.72190224 | 0.30147165 |
| N | 2.57547984 | -0.42812239 | -0.37877977 |
| N | 2.07580310 | 2.23913273 | -0.46042168 |
| N | 2.23918059 | 0.83638257 | 1.89715526 |
| Si | -1.46099526 | -0.22574735 | 0.21506790 |

| | | | |
|---|---|---|---|
| Cl | -0.77563496 | -0.95082174 | -1.67986516 |
| Cl | -2.35879414 | 1.67363016 | 0.35800701 |
| Cl | -0.89976876 | -1.15812790 | 2.03940698 |
| H | -4.59359107 | -4.42135223 | 0.43903558 |
| H | -3.13266959 | -3.50636200 | 0.85703767 |
| H | -3.11294709 | -4.66442159 | -0.48958216 |
| C | 1.22393435 | 2.80636116 | -1.51056351 |
| C | 3.38827936 | 2.86392172 | -0.32868315 |
| C | 1.44391424 | 1.53081425 | 2.91793290 |
| C | 3.56863705 | 0.43377746 | 2.34910799 |
| C | 2.93418569 | -0.38895474 | -1.80130322 |
| C | 2.41134103 | -1.79962894 | 0.13441349 |
| H | 1.69304676 | -2.35829227 | -0.47809560 |
| H | 2.04299425 | -1.78706826 | 1.16156898 |
| H | 3.38083757 | -2.31299849 | 0.10906861 |
| H | 4.12476861 | -0.03355403 | 1.53603990 |
| H | 3.47839164 | -0.28453296 | 3.17483648 |
| H | 4.13701989 | 1.30215298 | 2.71528468 |
| H | 0.24600098 | 2.32584257 | -1.50414363 |
| H | 1.68108430 | 2.68324574 | -2.50370127 |
| H | 1.08506023 | 3.87830466 | -1.32206591 |
| H | 2.14586845 | -0.82815663 | -2.42615272 |
| H | 3.86142243 | -0.95656105 | -1.94570754 |
| H | 3.10951001 | 0.63785062 | -2.12595679 |
| H | 0.44870308 | 1.76283423 | 2.53892401 |
| H | 1.94034529 | 2.46243251 | 3.22486967 |
| H | 1.33011136 | 0.88202599 | 3.79418061 |
| H | 3.93024227 | 2.44715331 | 0.52272844 |
| H | 3.26668974 | 3.94204048 | -0.16262917 |
| H | 4.00112050 | 2.72378919 | -1.23247006 |

Table B.70 90 degree enolate complex with substrate J.






90° O-Si-O enolate free energy: -3588.57204093860

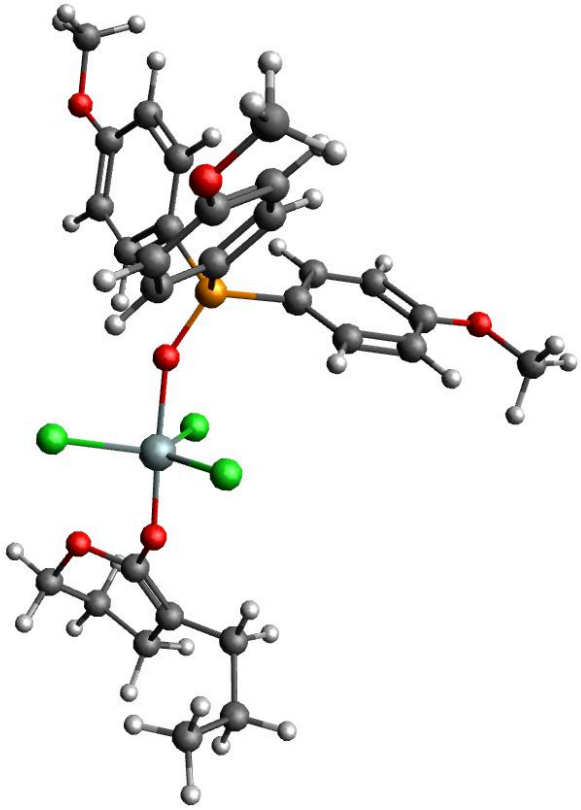
74

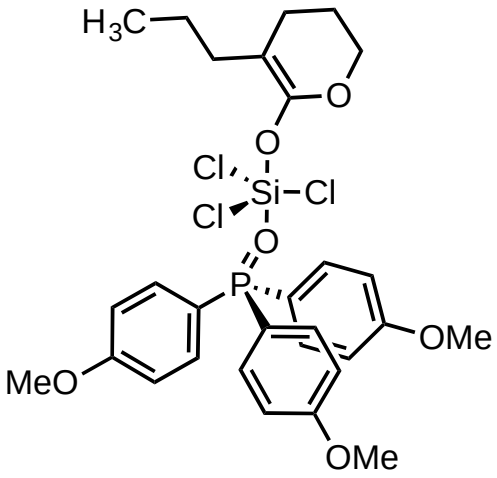
| | | | |
|---|---|---|---|
| C | 0.18136131 | -3.44998527 | 1.09854005 |
| C | 1.59390570 | -2.91433166 | 1.21892516 |
| C | -0.23411579 | -3.61144817 | -0.36935892 |
| C | 2.27583504 | -2.99972885 | 2.56393745 |
| O | 1.64176028 | -2.23093487 | -1.09919578 |
| H | -1.32083908 | -3.73224145 | -0.46476093 |
| H | 0.23951059 | -4.50251761 | -0.79972330 |
| C | 0.21873821 | -2.39012241 | -1.15871105 |
| H | -0.24880279 | -1.47605135 | -0.76018369 |
| H | -0.01406145 | -2.46913501 | -2.22408006 |
| C | 2.20532036 | -2.40183732 | 0.13603597 |
| O | 3.46263858 | -1.89186876 | 0.14405654 |
| H | 1.57795050 | -2.63795035 | 3.33866665 |
| H | -0.52606456 | -2.78623008 | 1.62388197 |
| H | 0.10863469 | -4.42175259 | 1.60713518 |
| C | 2.75464945 | -4.41244442 | 2.95964747 |
| P | 6.40902077 | 0.50909905 | -0.26676858 |
| O | 5.35103044 | -0.60591228 | -0.38322173 |
| C | 8.01725610 | 0.14635644 | -1.00380195 |
| C | 5.70480185 | 1.94978479 | -1.11075929 |
| C | 5.67200884 | 0.43992833 | 2.40372224 |
| C | 7.70521262 | 1.67140516 | 1.95591266 |
| C | 7.81880762 | 1.99524358 | 3.30968047 |
| C | 5.77462448 | 0.75795189 | 3.75013478 |
| C | 6.84739558 | 1.53828103 | 4.21319367 |
| H | 8.66155887 | 2.59035013 | 3.64309212 |

| | | | |
|---|---|---|---|
| H | 5.03861538 | 0.40426507 | 4.46571978 |
| O | 6.86027821 | 1.79236947 | 5.54830302 |
| C | 8.24251198 | 0.40782035 | -2.36342671 |
| C | 9.02406454 | -0.50757335 | -0.26469159 |
| C | 10.22176334 | -0.86422589 | -0.86395427 |
| C | 9.44139513 | 0.04733439 | -2.97806369 |
| H | 7.47415657 | 0.88969252 | -2.96050305 |
| H | 8.86024640 | -0.75343556 | 0.77941561 |
| C | 10.43855138 | -0.59173343 | -2.22620637 |
| H | 10.99958761 | -1.37324793 | -0.30326200 |
| O | 11.63883926 | -0.98686590 | -2.72088594 |
| H | 9.58041385 | 0.25800814 | -4.03214790 |
| C | 4.39981525 | 1.87574559 | -1.61124439 |
| C | 6.41226431 | 3.16132596 | -1.23053002 |
| H | 3.84303563 | 0.94804706 | -1.52400388 |
| C | 3.80362494 | 2.98172213 | -2.22288735 |
| C | 4.51703972 | 4.18204787 | -2.33611810 |
| C | 5.82983481 | 4.26438717 | -1.83650921 |
| H | 6.36816554 | 5.20222441 | -1.93487208 |
| H | 7.42890100 | 3.24622112 | -0.85449666 |
| H | 2.79175170 | 2.88990236 | -2.60103244 |
| O | 4.03280668 | 5.31669137 | -2.90750720 |
| C | 6.63972680 | 0.89356276 | 1.48687539 |
| H | 8.47253728 | 2.02508043 | 1.27204612 |
| H | 4.84738531 | -0.17397518 | 2.05407608 |
| Si | 4.87693745 | -2.40938808 | -0.60883859 |
| Cl | 4.25642268 | -4.48871309 | -0.85398495 |
| Cl | 6.51985738 | -2.93286728 | 0.63858800 |
| Cl | 5.24715456 | -2.14709912 | -2.67789858 |
| H | 3.13731234 | -2.32226944 | 2.58423478 |
| C | 11.91064544 | -0.79791453 | -4.10797476 |
| C | 7.92325458 | 2.56896894 | 6.09232261 |
| C | 2.70522331 | 5.31115327 | -3.42735221 |
| H | 7.71962728 | 2.63649693 | 7.16187147 |
| H | 7.94069498 | 3.57639133 | 5.65763439 |
| H | 8.89253075 | 2.07947180 | 5.93415789 |
| H | 12.90540120 | -1.21473132 | -4.27057092 |
| H | 11.91190028 | 0.26764563 | -4.36976538 |
| H | 11.18143944 | -1.33271631 | -4.72858973 |
| H | 2.54280038 | 6.31294993 | -3.82734122 |
| H | 1.97224493 | 5.10766240 | -2.63674777 |
| H | 2.59820791 | 4.57231133 | -4.23104224 |
| H | 1.90586662 | -5.11018778 | 2.93884142 |
| C | 3.40376522 | -4.44369105 | 4.34825617 |
| H | 3.46725588 | -4.76928026 | 2.20687011 |
| H | 2.70174446 | -4.11723100 | 5.12765740 |

| | | | |
|---|---|---|---|
| H | 4.27710403 | -3.77965935 | 4.38806185 |
| H | 3.74431804 | -5.45380187 | 4.60734003 |

Table B.71 180 degree enolate complex with substrate J.






180° O-Si-O enolate free energy: -3588.56754210316

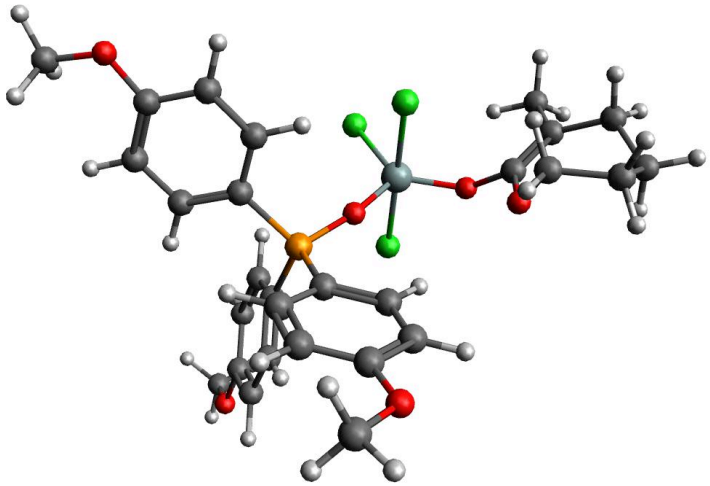
74

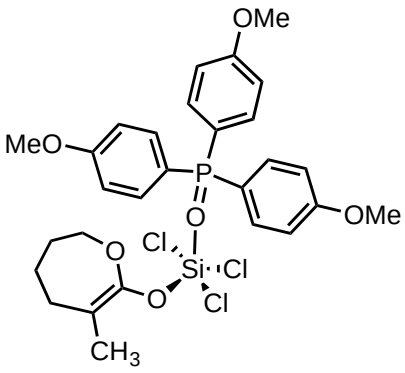
| | | | |
|---|---|---|---|
| C | -5.60226517 | -2.19255965 | -2.82957612 |
| C | -4.56489618 | -2.31753320 | -1.73168318 |
| C | -5.80802425 | -0.72950377 | -3.24364165 |
| C | -3.96913475 | -3.67969384 | -1.46578599 |
| O | -4.64938882 | 0.04505285 | -1.24079323 |
| H | -6.73135048 | -0.60351423 | -3.82403643 |
| H | -4.97330262 | -0.39442440 | -3.87286295 |
| C | -5.86079864 | 0.14470682 | -1.99683524 |
| H | -6.69936348 | -0.15253927 | -1.34831639 |
| H | -5.96269167 | 1.20748315 | -2.23391241 |
| C | -4.16224746 | -1.22159174 | -1.05573105 |
| O | -3.23465483 | -1.26057337 | -0.07835574 |
| H | -3.13847628 | -3.58394498 | -0.75875465 |
| H | -6.56480432 | -2.62981712 | -2.51738191 |
| H | -5.27913777 | -2.78229898 | -3.70123685 |

| | | | |
|---|---|---|---|
| C | -4.96463892 | -4.73254966 | -0.92564411 |
| P | 1.22100156 | 0.88131257 | 0.69689164 |
| O | -0.31516266 | 0.72848088 | 0.65205848 |
| C | 2.15853593 | -0.32641807 | -0.27269759 |
| C | 1.58333321 | 2.53524742 | 0.05129155 |
| C | 0.82842186 | 1.02134253 | 3.43905343 |
| C | 3.08547071 | 0.46045414 | 2.76651807 |
| C | 3.48664852 | 0.42811660 | 4.10469522 |
| C | 1.21691238 | 0.99010228 | 4.76976703 |
| C | 2.54856544 | 0.69704707 | 5.11227065 |
| H | 4.51536718 | 0.18378034 | 4.34370452 |
| H | 0.50288148 | 1.17749234 | 5.56574949 |
| O | 2.82610967 | 0.68943025 | 6.44284562 |
| C | 2.75742078 | 0.02582442 | -1.49779485 |
| C | 2.24998021 | -1.65743678 | 0.16385336 |
| C | 2.91739517 | -2.61837986 | -0.59431966 |
| C | 3.42901498 | -0.92168216 | -2.25697133 |
| H | 2.69161696 | 1.04576351 | -1.86345630 |
| H | 1.78287706 | -1.95945957 | 1.09574643 |
| C | 3.50963874 | -2.25208718 | -1.81281780 |
| H | 2.96037658 | -3.63938807 | -0.23322899 |
| O | 4.17901255 | -3.10678590 | -2.62871630 |
| H | 3.88960708 | -0.65836673 | -3.20410588 |
| C | 0.64828902 | 3.15224494 | -0.80185072 |
| C | 2.76860831 | 3.21235547 | 0.36227704 |
| H | -0.28233174 | 2.64627821 | -1.03790057 |
| C | 0.90691146 | 4.40646644 | -1.33683900 |
| C | 2.10289385 | 5.07572262 | -1.02761622 |
| C | 3.03755931 | 4.47516772 | -0.17001652 |
| H | 3.96126352 | 4.97663247 | 0.09510104 |
| H | 3.49656032 | 2.76596287 | 1.03484032 |
| H | 0.19139896 | 4.89206747 | -1.99330521 |
| O | 2.25976983 | 6.29789136 | -1.60170026 |
| C | 3.44219219 | 7.04343297 | -1.32887058 |
| H | 3.34218109 | 7.97021879 | -1.89548212 |
| H | 4.33761326 | 6.50458696 | -1.66370548 |
| H | 3.52701137 | 7.27513782 | -0.25958008 |
| C | 4.23694377 | -4.48879220 | -2.28239125 |
| H | 4.78089485 | -4.97179909 | -3.09521502 |
| H | 3.23041012 | -4.91787227 | -2.20641241 |
| H | 4.77745620 | -4.63955532 | -1.33949165 |
| C | 4.14841573 | 0.37908541 | 6.87080684 |
| H | 4.43768648 | -0.63365128 | 6.56241312 |
| H | 4.12534008 | 0.43506928 | 7.95999838 |
| H | 4.87286333 | 1.10608188 | 6.48211973 |
| C | 1.76341642 | 0.76145951 | 2.41767791 |

| | | | |
|---|---|---|---|
| H | 3.81705450 | 0.22986557 | 1.99634758 |
| H | -0.20635055 | 1.22748386 | 3.18182459 |
| Si | -1.87177993 | -0.28098253 | 0.25591830 |
| Cl | -2.90686530 | 1.27666526 | 1.22629082 |
| Cl | -1.10694482 | -1.80385658 | 1.52913369 |
| Cl | -1.28069257 | -0.11353917 | -1.79129350 |
| H | -3.54141510 | -4.06955658 | -2.40518498 |
| H | -5.78451320 | -4.87359965 | -1.64520641 |
| C | -5.54200895 | -4.38569691 | 0.45161991 |
| H | -4.44264078 | -5.69893269 | -0.86855555 |
| H | -6.11307571 | -3.45027117 | 0.42052897 |
| H | -4.74090757 | -4.25261958 | 1.18951536 |
| H | -6.21025751 | -5.17760049 | 0.81377508 |

Table B.72 120 degree enolate complex with substrate I.






120° O-Si-O enolate free energy: -3549.24131119656

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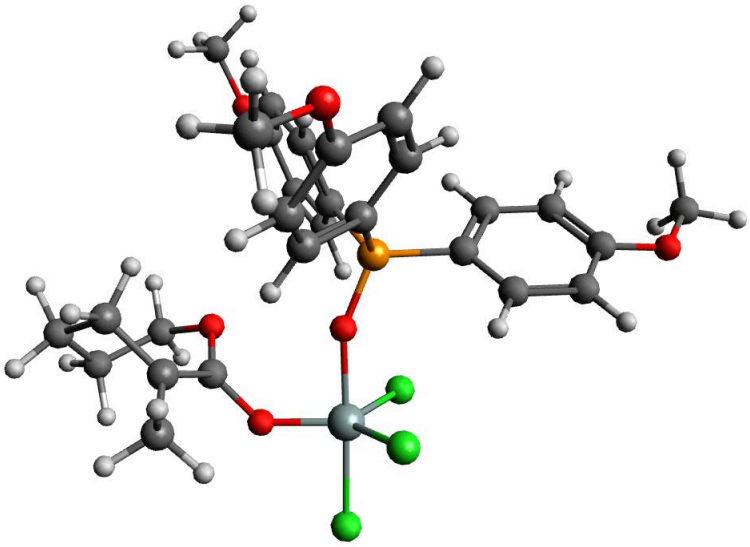
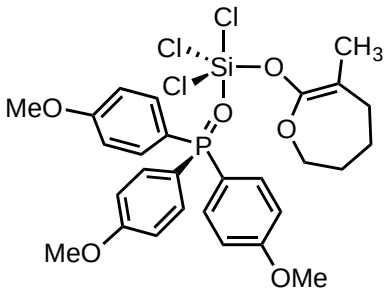
| | | | |
|---|---|---|---|
| C | 0.97245116 | -0.36035206 | -1.36582407 |
| O | 2.51498726 | 1.42497990 | -1.96543678 |
| C | 1.62241889 | 2.48444748 | -1.57679425 |
| C | 2.19986695 | 0.17096741 | -1.50290910 |
| O | 3.33611591 | -0.54718616 | -1.28936553 |
| P | 7.06450690 | 1.47443931 | 0.11132820 |
| O | 5.70049163 | 0.74873709 | -0.08662696 |
| C | 8.45461765 | 0.56934046 | -0.58647670 |
| C | 6.87721632 | 3.05335739 | -0.73836530 |
| C | 6.28140516 | 2.17852941 | 2.67612788 |
| C | 8.60489654 | 1.51773814 | 2.46204272 |
| C | 8.79768452 | 1.72354234 | 3.83032969 |
| C | 6.46732286 | 2.38986573 | 4.03164476 |
| C | 7.72182969 | 2.15187912 | 4.62213301 |

| | | | |
|---|---|---|---|
| H | 9.77528164 | 1.53767231 | 4.26096558 |
| H | 5.64662178 | 2.71516537 | 4.66301041 |
| O | 7.78550078 | 2.35843870 | 5.96161528 |
| C | 9.25360880 | 1.12548358 | -1.60359115 |
| C | 8.72191965 | -0.73851446 | -0.15068297 |
| C | 9.76181815 | -1.47863855 | -0.70769731 |
| C | 10.29592027 | 0.39767254 | -2.15981814 |
| H | 9.05381561 | 2.12693780 | -1.97105304 |
| H | 8.10335342 | -1.20062262 | 0.61305603 |
| C | 10.55142407 | -0.91264840 | -1.72145995 |
| H | 9.92894911 | -2.49310672 | -0.36460710 |
| O | 11.57818876 | -1.55008784 | -2.33830348 |
| H | 10.91265543 | 0.81388248 | -2.95029401 |
| C | 5.94555825 | 3.16868292 | -1.78924421 |
| C | 7.65593111 | 4.16301782 | -0.38591662 |
| H | 5.31187289 | 2.32778493 | -2.05481587 |
| C | 5.81486676 | 4.36743023 | -2.47429444 |
| C | 6.60420806 | 5.47573040 | -2.12184355 |
| C | 7.52899442 | 5.37270838 | -1.07128817 |
| H | 8.14106037 | 6.21731238 | -0.77675610 |
| H | 8.36563588 | 4.09767952 | 0.43536420 |
| H | 5.09922727 | 4.47117316 | -3.28324913 |
| O | 6.39467263 | 6.60251452 | -2.84982465 |
| C | 7.14377400 | 7.77561140 | -2.54271075 |
| H | 6.80179814 | 8.53467827 | -3.24774818 |
| H | 8.21922768 | 7.60563936 | -2.67976823 |
| H | 6.94756922 | 8.11175671 | -1.51671948 |
| C | 11.81512772 | -2.92655090 | -2.04306281 |
| H | 12.62653991 | -3.23223308 | -2.70499021 |
| H | 10.92272933 | -3.52925197 | -2.24983753 |
| H | 12.12390867 | -3.05982900 | -0.99878046 |
| C | 8.98640806 | 2.03683509 | 6.65887890 |
| H | 9.25484689 | 0.98320047 | 6.51445907 |
| H | 8.77035824 | 2.21612501 | 7.71317155 |
| H | 9.81552009 | 2.68010146 | 6.33913731 |
| C | 7.35242541 | 1.73271205 | 1.87118715 |
| H | 9.44306365 | 1.17574373 | 1.86240379 |
| H | 5.29474793 | 2.31806603 | 2.24516600 |
| Si | 4.51637189 | -0.51725999 | -0.10371221 |
| Cl | 5.79404359 | -1.68911921 | -1.48715165 |
| Cl | 3.27677654 | 0.78967561 | 1.26645682 |
| Cl | 4.70917930 | -1.97625532 | 1.42268663 |
| C | -0.30868059 | 0.30903575 | -1.83425586 |
| H | -0.97328855 | -0.49593712 | -2.18038301 |
| C | -0.16620222 | 1.32495367 | -2.97897500 |
| H | -0.84070044 | 0.76710938 | -0.98233709 |

| | | | |
|---|---|---|---|
| C | 0.78671814 | -1.71603574 | -0.73122985 |
| C | 0.47349430 | 2.66400588 | -2.56822529 |
| H | 2.24310019 | 3.38540596 | -1.52425295 |
| H | 1.25543113 | 2.26504081 | -0.56872237 |
| H | 0.82889316 | 3.18699848 | -3.46604957 |
| H | -0.27512309 | 3.31927722 | -2.09806280 |
| H | -1.15627495 | 1.52045219 | -3.41276318 |
| H | 0.43469159 | 0.86509362 | -3.77393425 |
| H | 1.72179700 | -2.13198953 | -0.35188289 |
| H | 0.36558685 | -2.43341863 | -1.45158551 |
| H | 0.07896463 | -1.65761167 | 0.10933476 |

Table B.73 90 degree enolate complex with substrate I.






90° O-Si-O enolate free energy: -3549.24282952922

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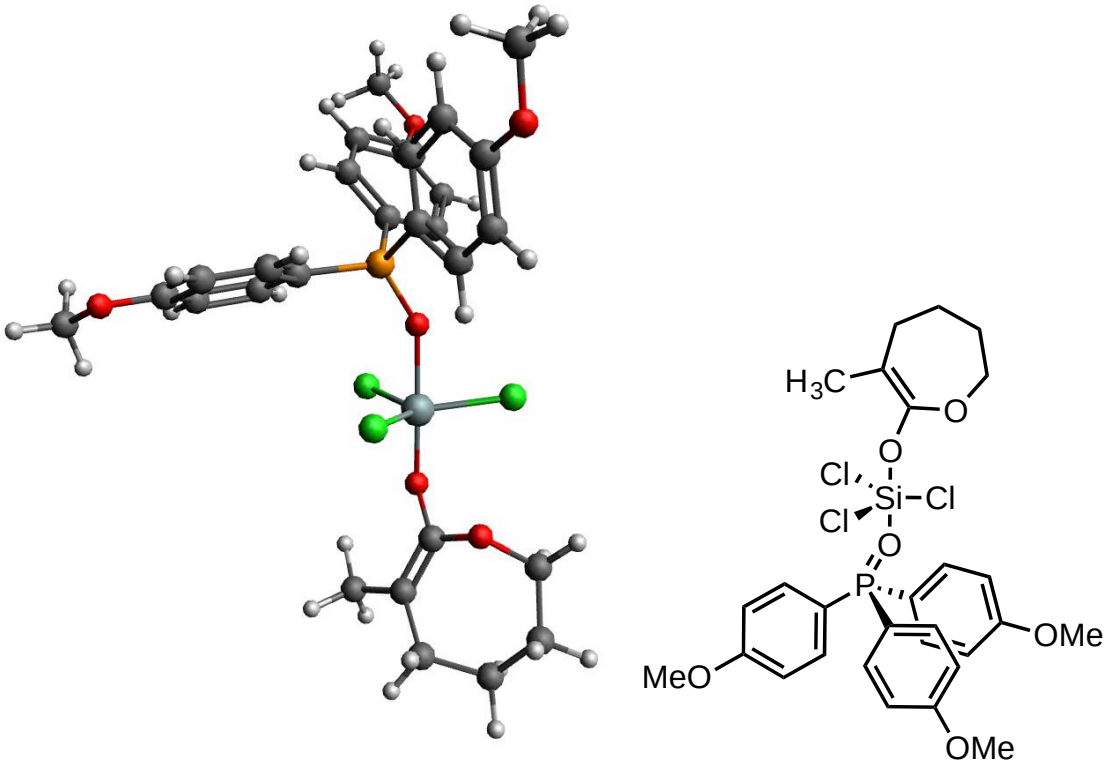
| | | | |
|---|---|---|---|
| C | 2.46519036 | -3.16185969 | -2.71275826 |
| C | 2.53465847 | -2.13798800 | -0.36453945 |
| C | 3.43556768 | -4.22007208 | -2.15293272 |
| C | 1.32346053 | -2.06255835 | 0.52564352 |
| O | 4.81197116 | -2.62076536 | -0.78838240 |
| H | 3.59237536 | -5.01056631 | -2.89995520 |
| H | 2.97905581 | -4.71084668 | -1.28551678 |
| C | 4.81676406 | -3.70420560 | -1.75289765 |
| H | 5.35559004 | -3.29671372 | -2.61556587 |
| H | 5.41085490 | -4.52781426 | -1.33429686 |
| C | 3.74484679 | -2.53215686 | 0.06814163 |
| O | 4.00285499 | -2.93919846 | 1.33882960 |
| H | 0.87616670 | -1.05688644 | 0.50755399 |
| H | 0.53867571 | -2.75592805 | 0.18666970 |

| | | | |
|---|---|---|---|
| P | 6.14950579 | 0.39445976 | 1.06955737 |
| O | 5.31315666 | -0.82943766 | 1.50205605 |
| C | 7.00311261 | 0.05960252 | -0.49272719 |
| C | 5.00792085 | 1.77757593 | 0.82720721 |
| C | 6.95883239 | 1.18946343 | 3.60899691 |
| C | 8.73064386 | 1.07966176 | 1.96676571 |
| C | 9.65570491 | 1.49998014 | 2.92638565 |
| C | 7.86781800 | 1.60597834 | 4.56734289 |
| C | 9.22575054 | 1.76198765 | 4.23403715 |
| H | 10.69620415 | 1.61116050 | 2.64304780 |
| H | 7.55328408 | 1.80594373 | 5.58701430 |
| O | 10.03689784 | 2.17015497 | 5.24412494 |
| C | 6.89386314 | 0.92478256 | -1.58688179 |
| C | 7.78680661 | -1.10537981 | -0.62545541 |
| C | 8.44861181 | -1.37799775 | -1.81263227 |
| C | 7.55347471 | 0.65633698 | -2.78996431 |
| H | 6.28381757 | 1.82053441 | -1.52108069 |
| H | 7.86441688 | -1.80632897 | 0.20008890 |
| C | 8.33795739 | -0.49840867 | -2.90492805 |
| H | 9.04960274 | -2.27562350 | -1.92354958 |
| O | 9.02020686 | -0.85856231 | -4.02480780 |
| H | 7.43908127 | 1.34573318 | -3.61866543 |
| C | 3.65845069 | 1.51439646 | 0.56017230 |
| C | 5.44599027 | 3.11421862 | 0.88487011 |
| H | 3.30546737 | 0.48772869 | 0.53008228 |
| C | 2.75640148 | 2.55835600 | 0.34453544 |
| C | 3.20573152 | 3.88599367 | 0.39437280 |
| C | 4.55781147 | 4.15833551 | 0.66789628 |
| H | 4.88281006 | 5.19315560 | 0.71630420 |
| H | 6.48422304 | 3.33943703 | 1.11374180 |
| H | 1.71596606 | 2.32558198 | 0.14922314 |
| O | 2.41536140 | 4.97451257 | 0.19896870 |
| C | 7.37918470 | 0.91318760 | 2.29079123 |
| H | 9.08255220 | 0.87922662 | 0.95953853 |
| H | 5.91751191 | 1.05745922 | 3.88711090 |
| Si | 4.91763829 | -2.31647043 | 2.59903127 |
| Cl | 7.01443417 | -2.63253673 | 2.78571273 |
| Cl | 3.98118161 | -0.95586819 | 3.93994220 |
| Cl | 4.43662447 | -4.05409066 | 3.80814123 |
| H | 1.56303212 | -2.30985817 | 1.56282563 |
| C | 8.93401015 | -0.02915990 | -5.18006342 |
| C | 11.43310542 | 2.30742539 | 4.99500525 |
| C | 1.02700785 | 4.78016048 | -0.06022635 |
| H | 11.86962658 | 2.62811822 | 5.94185375 |
| H | 11.62623678 | 3.06631828 | 4.22634277 |
| H | 11.87541423 | 1.35023438 | 4.69215502 |

| | | | |
|---|---|---|---|
| H | 9.54568056 | -0.51879270 | -5.93910845 |
| H | 9.33205586 | 0.97356305 | -4.97960143 |
| H | 7.89880973 | 0.04744322 | -5.53577283 |
| H | 0.60852196 | 5.78053722 | -0.17901695 |
| H | 0.53498010 | 4.27354186 | 0.77926542 |
| H | 0.87312684 | 4.20588147 | -0.98236185 |
| C | 2.39365711 | -1.87082628 | -1.85135122 |
| H | 1.46988065 | -3.62091347 | -2.77998384 |
| H | 2.75149027 | -2.89073403 | -3.73882331 |
| H | 3.19742436 | -1.19470152 | -2.17153642 |
| H | 1.44768552 | -1.35101836 | -2.05183254 |

Table B.74 180 degree enolate complex with substrate I.




180° O-Si-O enolate free energy: -3549.24773574247

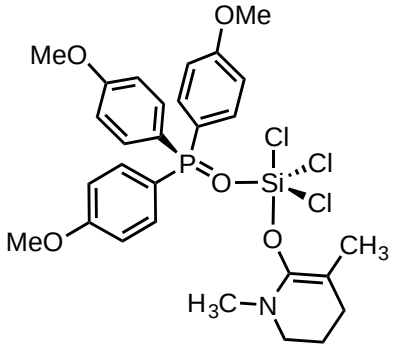
71

| | | | |
|---|---|---|---|
| C | -5.41508768 | -2.72646123 | -3.17201916 |
| C | -4.39656064 | -2.79980872 | -2.04773457 |
| C | -6.59553032 | -0.47521033 | -2.69801952 |
| C | -3.93764382 | -4.16835766 | -1.61264497 |
| O | -4.27955875 | -0.41668316 | -1.86146885 |
| C | -5.63921033 | -0.03464152 | -1.59378533 |
| H | -5.94206172 | -0.44108218 | -0.61929896 |
| H | -5.61579680 | 1.05749385 | -1.51792247 |

| | | | |
|---|---|---|---|
| C | -3.90765669 | -1.68204509 | -1.48119062 |
| O | -2.99504682 | -1.71584678 | -0.47740483 |
| P | 1.23502221 | 0.71730030 | 0.59165701 |
| O | -0.28531814 | 0.46851616 | 0.47273437 |
| C | 2.29367061 | -0.41131833 | -0.34679888 |
| C | 1.51636627 | 2.40267309 | -0.01121858 |
| C | 0.70546449 | 0.80298809 | 3.31275224 |
| C | 3.02211072 | 0.38883539 | 2.74649517 |
| C | 3.36002853 | 0.37049684 | 4.10235961 |
| C | 1.03072789 | 0.78561372 | 4.66053931 |
| C | 2.35999395 | 0.57200229 | 5.06508995 |
| H | 4.38947449 | 0.19038803 | 4.39020072 |
| H | 0.26933625 | 0.92299104 | 5.42210479 |
| O | 2.57351516 | 0.57063828 | 6.40753395 |
| C | 2.87724030 | -0.01379230 | -1.56595036 |
| C | 2.49223804 | -1.72819971 | 0.09681953 |
| C | 3.25106446 | -2.63071805 | -0.64703159 |
| C | 3.63706377 | -0.90298273 | -2.31165572 |
| H | 2.72933648 | 0.99489789 | -1.93880741 |
| H | 2.03750656 | -2.06750815 | 1.02208777 |
| C | 3.82694910 | -2.21928621 | -1.85868129 |
| H | 3.37628458 | -3.64320388 | -0.28121646 |
| O | 4.58142217 | -3.01567203 | -2.65903869 |
| H | 4.08536265 | -0.60539130 | -3.25451191 |
| C | 0.55759174 | 2.99155418 | -0.85730554 |
| C | 2.65973882 | 3.13375223 | 0.33249452 |
| H | -0.34083335 | 2.44121585 | -1.11854317 |
| C | 0.75140814 | 4.27380024 | -1.35280611 |
| C | 1.90518617 | 4.99815120 | -1.00996702 |
| C | 2.86337560 | 4.42435702 | -0.15978432 |
| H | 3.75501142 | 4.96785332 | 0.13101737 |
| H | 3.40530464 | 2.70826769 | 0.99926596 |
| H | 0.01705739 | 4.73760262 | -2.00418933 |
| O | 2.00076126 | 6.24448515 | -1.54474109 |
| C | 3.14050473 | 7.04142211 | -1.23930253 |
| H | 2.99717809 | 7.97859832 | -1.77893351 |
| H | 4.06521839 | 6.55976112 | -1.58182817 |
| H | 3.20543659 | 7.24500590 | -0.16288380 |
| C | 4.77013291 | -4.38103236 | -2.29469588 |
| H | 5.37561320 | -4.81567585 | -3.09114859 |
| H | 3.81073184 | -4.90908899 | -2.23198491 |
| H | 5.30411245 | -4.46661578 | -1.33992905 |
| C | 3.88921500 | 0.33454431 | 6.89813741 |
| H | 4.25421715 | -0.65445763 | 6.59328733 |
| H | 3.80866028 | 0.37361078 | 7.98535069 |
| H | 4.58667152 | 1.10933890 | 6.55488815 |

| | | | |
|---|---|---|---|
| C | 1.70194589 | 0.60893018 | 2.33584118 |
| H | 3.80252671 | 0.21179497 | 2.01108627 |
| H | -0.32605923 | 0.94944908 | 3.00711137 |
| Si | -1.72508695 | -0.65908786 | -0.05353067 |
| Cl | -2.93811335 | 0.81504625 | 0.86197944 |
| Cl | -0.92695221 | -2.14316036 | 1.24178939 |
| Cl | -0.99253399 | -0.44093324 | -2.04334787 |
| H | -4.78026946 | -4.77223237 | -1.24171943 |
| H | -3.18618076 | -4.10956913 | -0.82200513 |
| H | -3.50399586 | -4.72293508 | -2.45912225 |
| C | -6.73529411 | -1.99691078 | -2.84738225 |
| H | -7.45677926 | -2.20141594 | -3.65145338 |
| H | -7.16205602 | -2.41906244 | -1.92551223 |
| H | -5.65956086 | -3.75397267 | -3.47136296 |
| H | -4.96440939 | -2.25264405 | -4.05951265 |
| H | -6.25095365 | -0.04061246 | -3.64743583 |
| H | -7.58110845 | -0.03349003 | -2.48703569 |

Table B.75 90 degree enolate complex (swapped) with substrate H.




90° O-Si-O enolate free energy: -3529.36725088155

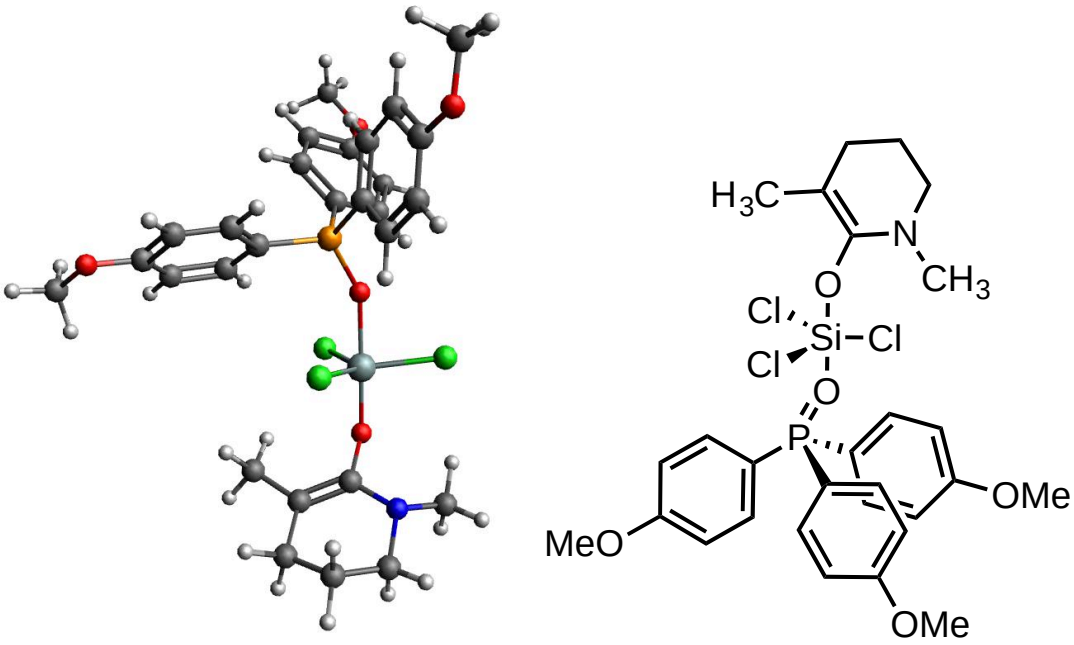
72

| | | | |
|---|---|---|---|
| C | 0.92001729 | -3.68928003 | -0.32279434 |
| C | 2.41822642 | -3.79864725 | -0.11852308 |
| C | 0.52026442 | -2.54339063 | -1.25909272 |
| C | 2.89240761 | -5.05083736 | 0.57029534 |
| N | 2.82876158 | -1.60528540 | -1.14119903 |
| H | -0.54154304 | -2.29008943 | -1.14194765 |
| H | 0.66501421 | -2.84309023 | -2.30560203 |
| C | 1.40092393 | -1.32744789 | -0.94994576 |
| H | 1.25440697 | -1.02924763 | 0.09741826 |
| H | 1.13608243 | -0.46757829 | -1.57856825 |
| C | 3.25573731 | -2.81626785 | -0.51707818 |
| O | 4.60925768 | -2.92721209 | -0.45109290 |
| H | 2.60470357 | -5.06580275 | 1.63229078 |
| H | 0.43012205 | -3.55663008 | 0.65725151 |

| | | | |
|---|---|---|---|
| H | 0.53645405 | -4.64347511 | -0.71316388 |
| H | 2.43621650 | -5.93457889 | 0.10101452 |
| P | 6.80118100 | 0.43596283 | 0.06040484 |
| O | 5.95190118 | -0.88354811 | 0.15528929 |
| C | 8.11904352 | 0.22455473 | -1.15106708 |
| C | 5.63398871 | 1.70657743 | -0.47018417 |
| C | 6.58322553 | 1.18636647 | 2.71424178 |
| C | 8.82756040 | 1.29327800 | 1.81439753 |
| C | 9.30412080 | 1.75443680 | 3.04379268 |
| C | 7.04644593 | 1.63778447 | 3.93719406 |
| C | 8.41391766 | 1.91965434 | 4.11316887 |
| H | 10.36151674 | 1.96531095 | 3.15494923 |
| H | 6.37395614 | 1.76577340 | 4.77950755 |
| O | 8.77068012 | 2.34529693 | 5.35220443 |
| C | 8.16123774 | 0.98592790 | -2.32690554 |
| C | 9.09588417 | -0.77587866 | -0.94745147 |
| C | 10.08982820 | -0.98392161 | -1.88953371 |
| C | 9.16088043 | 0.78033727 | -3.28035951 |
| H | 7.40678803 | 1.74256881 | -2.51792644 |
| H | 9.05971709 | -1.40353439 | -0.06132451 |
| C | 10.13295864 | -0.20640045 | -3.06086450 |
| H | 10.83710568 | -1.75834733 | -1.74774296 |
| O | 11.14679968 | -0.49132178 | -3.91639987 |
| H | 9.16614636 | 1.38309493 | -4.18120700 |
| C | 4.30706779 | 1.37265909 | -0.76155741 |
| C | 6.03298822 | 3.05846778 | -0.52357861 |
| H | 3.97024340 | 0.33859290 | -0.69688474 |
| C | 3.38998584 | 2.36618650 | -1.11777997 |
| C | 3.79861133 | 3.70385197 | -1.18974802 |
| C | 5.13109588 | 4.04499035 | -0.88952061 |
| H | 5.42686790 | 5.08856147 | -0.93607979 |
| H | 7.04981595 | 3.34421859 | -0.26510331 |
| H | 2.36523145 | 2.08070763 | -1.32607199 |
| O | 2.98923785 | 4.74177034 | -1.52644687 |
| C | 7.47263792 | 0.99849086 | 1.63610298 |
| H | 9.53177553 | 1.15407140 | 1.00054384 |
| H | 5.52759519 | 0.95591551 | 2.60140962 |
| Si | 5.84509679 | -2.55346119 | 0.67793493 |
| Cl | 7.05526626 | -3.97766358 | -0.36180603 |
| Cl | 4.58558512 | -2.70562967 | 2.38883174 |
| Cl | 7.61915097 | -2.23646151 | 2.08095242 |
| H | 3.97694599 | -5.16584907 | 0.51756277 |
| C | 11.24913719 | 0.23534947 | -5.13829878 |
| C | 10.14666736 | 2.59465527 | 5.62610928 |
| C | 1.62147140 | 4.47735283 | -1.83189258 |
| H | 10.18836105 | 2.88698721 | 6.67621384 |

| | | | |
|---|---|---|---|
| H | 10.53336353 | 3.41088415 | 5.00286947 |
| H | 10.74909737 | 1.69097417 | 5.47171980 |
| H | 12.12261722 | -0.17200994 | -5.64892536 |
| H | 11.39967484 | 1.30597286 | -4.95074087 |
| H | 10.35834116 | 0.08867129 | -5.76163038 |
| H | 1.18080218 | 5.44746270 | -2.06538239 |
| H | 1.10247966 | 4.03513909 | -0.97255477 |
| H | 1.53171149 | 3.81441255 | -2.70132485 |
| C | 3.27504692 | -1.49684787 | -2.53712268 |
| H | 3.09850930 | -0.47724387 | -2.89930883 |
| H | 2.75697797 | -2.20331382 | -3.20767152 |
| H | 4.34565530 | -1.70511747 | -2.58499646 |

Table B.76 180 degree enolate complex with substrate H.




180° O-Si-O enolate free energy: -3529.37765932042

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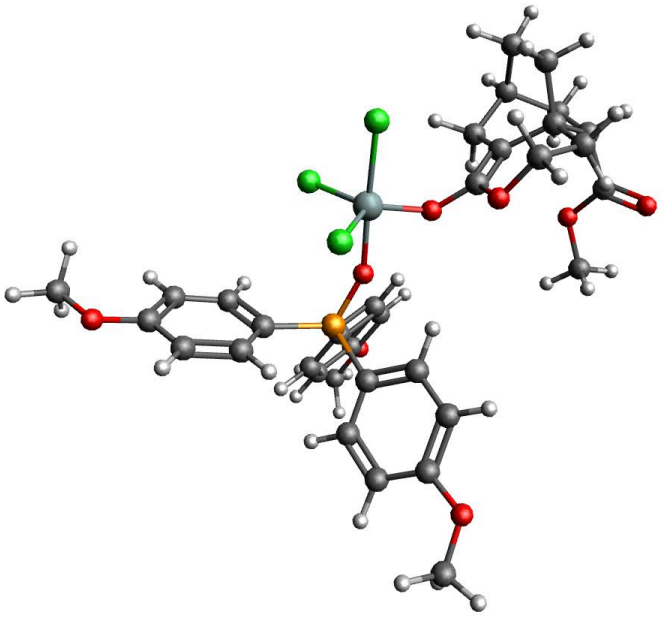
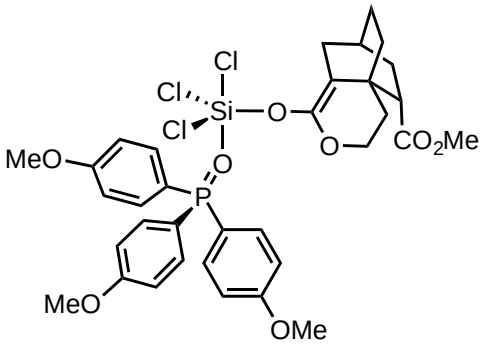
| | | | |
|---|---|---|---|
| C | -4.55033531 | -2.46911744 | -3.55999430 |
| C | -3.87957825 | -2.18755374 | -2.23251866 |
| C | -5.20560397 | -1.20540629 | -4.12563050 |
| C | -2.81361789 | -3.15935847 | -1.80612313 |
| N | -5.14986678 | -0.11365504 | -1.90992051 |
| H | -5.86670718 | -1.44273987 | -4.96907004 |
| H | -4.43239452 | -0.51834712 | -4.49282556 |
| C | -6.00458466 | -0.51306868 | -3.02800095 |
| H | -6.80204317 | -1.19614100 | -2.67256991 |
| H | -6.49768926 | 0.39004793 | -3.40913763 |
| C | -4.16860452 | -1.06175378 | -1.53818218 |

| | | | |
|---|---|---|---|
| O | -3.51146457 | -0.73921513 | -0.38410545 |
| H | -5.29481646 | -3.27793112 | -3.46735682 |
| H | -3.79456149 | -2.84365477 | -4.26827353 |
| P | 1.11664720 | 0.99332085 | 0.50955592 |
| O | -0.42360092 | 0.94008712 | 0.43842538 |
| C | 1.96595062 | -0.27001291 | -0.46796846 |
| C | 1.62630590 | 2.62471855 | -0.08986211 |
| C | 0.72222467 | 1.17700908 | 3.24974192 |
| C | 2.89744506 | 0.34315077 | 2.59144114 |
| C | 3.28166061 | 0.25894317 | 3.93250504 |
| C | 1.09298288 | 1.09446126 | 4.58323404 |
| C | 2.37639264 | 0.63966365 | 4.93403851 |
| H | 4.27036278 | -0.11073327 | 4.17901504 |
| H | 0.40098683 | 1.36555993 | 5.37461094 |
| O | 2.64206028 | 0.59763144 | 6.26642089 |
| C | 2.76480727 | 0.06051695 | -1.57836249 |
| C | 1.79432243 | -1.62311662 | -0.13791610 |
| C | 2.40240251 | -2.62862510 | -0.88767258 |
| C | 3.37877857 | -0.93316138 | -2.32876711 |
| H | 2.90172319 | 1.09897484 | -1.86342673 |
| H | 1.16213203 | -1.90117814 | 0.70003523 |
| C | 3.19966323 | -2.28474070 | -1.99072656 |
| H | 2.23801302 | -3.66417131 | -0.61289559 |
| O | 3.83573633 | -3.18179750 | -2.78783622 |
| H | 3.99309760 | -0.68741682 | -3.18958401 |
| C | 0.88123772 | 3.24464828 | -1.11291517 |
| C | 2.74464196 | 3.28674443 | 0.43006269 |
| H | -0.00075405 | 2.75449733 | -1.51351723 |
| C | 1.25999191 | 4.48549277 | -1.60489527 |
| C | 2.38768974 | 5.14110278 | -1.08079132 |
| C | 3.13237967 | 4.53740592 | -0.05703657 |
| H | 3.99879389 | 5.02837321 | 0.37130255 |
| H | 3.32223172 | 2.84101160 | 1.23509578 |
| H | 0.68924772 | 4.97350069 | -2.38902865 |
| O | 2.67040880 | 6.35456766 | -1.62391931 |
| C | 3.78315502 | 7.09125335 | -1.12506190 |
| H | 3.79802374 | 8.02162844 | -1.69442757 |
| H | 4.72279418 | 6.54769037 | -1.28628715 |
| H | 3.66255250 | 7.31622388 | -0.05792079 |
| C | 3.66759704 | -4.57431810 | -2.53109198 |
| H | 4.24508602 | -5.08587547 | -3.30226089 |
| H | 2.61302214 | -4.86604648 | -2.60707410 |
| H | 4.05741188 | -4.84380254 | -1.54150183 |
| C | 3.91702951 | 0.13602629 | 6.70209230 |
| H | 4.08902108 | -0.90287348 | 6.39369249 |
| H | 3.89368798 | 0.19350784 | 7.79119282 |

| | | | |
|---|---|---|---|
| H | 4.72229205 | 0.77530747 | 6.31833455 |
| C | 1.62594447 | 0.80705920 | 2.23450098 |
| H | 3.59966790 | 0.02811417 | 1.82388511 |
| H | -0.27749690 | 1.50851524 | 2.98558796 |
| Si | -2.06062313 | 0.08238309 | -0.02305402 |
| Cl | -2.96433820 | 1.82128873 | 0.77032665 |
| Cl | -1.54733251 | -1.39176582 | 1.43524792 |
| Cl | -1.32237726 | 0.11779412 | -2.02557085 |
| H | -3.18079922 | -4.19228570 | -1.90595021 |
| H | -2.50929289 | -3.01279858 | -0.76741816 |
| H | -1.91364673 | -3.08251396 | -2.43887391 |
| C | -5.94458197 | 0.45601333 | -0.82140518 |
| H | -6.50520067 | 1.31277216 | -1.21196375 |
| H | -5.30220838 | 0.80013305 | -0.01455947 |
| H | -6.66731339 | -0.27602461 | -0.41360342 |

Table B.77 90 degree enolate complex with substrate K.






-3931.97786711196

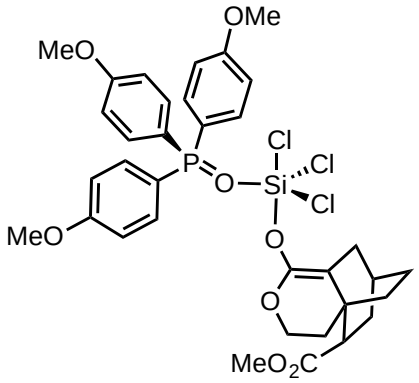
85

| | | | |
|---|---|---|---|
| C | -0.07431491 | -0.57922060 | -1.86082121 |
| C | 1.30603943 | -0.64036189 | -1.23022639 |
| C | -0.61823696 | 0.86300486 | -1.85248952 |
| C | 1.95528872 | -2.01018540 | -1.25313913 |
| O | 1.26752268 | 1.65856424 | -0.52680568 |
| C | -0.16729877 | 1.60265437 | -0.59569788 |
| C | 1.85813795 | 0.43192866 | -0.64891516 |
| O | 3.12970590 | 0.44954108 | -0.18005348 |

| | | | |
|---|---|---|---|
| H | 2.28905621 | -2.29788977 | -0.24707577 |
| C | -1.00578053 | -1.53430943 | -1.05776934 |
| C | -0.01114503 | -1.19469131 | -3.31469239 |
| C | 0.91151996 | -3.01703469 | -1.77711794 |
| P | 6.66351237 | 1.76898368 | 0.56206168 |
| O | 5.25916397 | 1.13248429 | 0.51637572 |
| C | 7.71794086 | 0.73650792 | -0.48902919 |
| C | 6.54389913 | 3.42920911 | -0.15103154 |
| C | 7.34570924 | 3.06008546 | 2.96198185 |
| C | 8.00371265 | 0.73934295 | 2.77231863 |
| C | 8.51636117 | 0.76952544 | 4.06842762 |
| C | 7.85714294 | 3.10216074 | 4.24987082 |
| C | 8.44457396 | 1.95641569 | 4.81353445 |
| H | 8.95079663 | -0.13082016 | 4.48692337 |
| H | 7.79794438 | 4.00646639 | 4.84753629 |
| O | 8.90925556 | 2.09520270 | 6.08089735 |
| C | 7.10569957 | -0.15489258 | -1.39073017 |
| C | 9.11415754 | 0.83905022 | -0.47959399 |
| C | 9.89803134 | 0.07526963 | -1.34742801 |
| C | 7.87578028 | -0.91856745 | -2.25667006 |
| H | 6.02425590 | -0.25058574 | -1.39883116 |
| H | 9.61149522 | 1.50779265 | 0.21829833 |
| C | 9.27622647 | -0.80682380 | -2.24388320 |
| H | 10.97721186 | 0.17041426 | -1.31120366 |
| O | 9.94039375 | -1.59573633 | -3.12990048 |
| H | 7.41393639 | -1.61560705 | -2.94926675 |
| C | 5.31895107 | 3.84975961 | -0.70240597 |
| C | 7.65010097 | 4.28542791 | -0.22164380 |
| H | 4.45188777 | 3.19932252 | -0.65341431 |
| C | 5.21121358 | 5.09654505 | -1.30289670 |
| C | 6.32398713 | 5.95123614 | -1.36625988 |
| C | 7.55139515 | 5.54211906 | -0.82082029 |
| H | 8.42420967 | 6.18410398 | -0.85364491 |
| H | 8.60673419 | 3.98398656 | 0.19808260 |
| H | 4.26903784 | 5.43252950 | -1.72486574 |
| O | 6.11425953 | 7.14951999 | -1.97245048 |
| C | 7.18803390 | 8.08135571 | -2.05341199 |
| H | 6.78026010 | 8.95540884 | -2.56305594 |
| H | 8.02407323 | 7.67508931 | -2.63668787 |
| H | 7.53817643 | 8.37002860 | -1.05421316 |
| C | 11.36283758 | -1.53764655 | -3.17480000 |
| H | 11.66109042 | -2.24327047 | -3.95139534 |
| H | 11.80247987 | -1.84060346 | -2.21596904 |
| H | 11.71027753 | -0.53119030 | -3.44054717 |
| C | 9.47313644 | 0.96263533 | 6.73934537 |
| H | 8.74270156 | 0.14855124 | 6.81929027 |

| | | | |
|---|---|---|---|
| H | 9.74443624 | 1.30978607 | 7.73715833 |
| H | 10.37079598 | 0.60799403 | 6.21738451 |
| C | 7.42141559 | 1.87925758 | 2.19662002 |
| H | 8.04330035 | -0.19288141 | 2.21685407 |
| H | 6.86984447 | 3.94618318 | 2.55433671 |
| Si | 3.70301341 | 0.58052743 | 1.40081729 |
| H | 2.84553397 | -2.02094872 | -1.89922616 |
| Cl | 4.82888512 | -1.03369813 | 2.20131620 |
| Cl | 3.72642120 | 2.40938333 | 2.47898349 |
| Cl | 1.84874487 | -0.09192376 | 2.35806962 |
| H | -1.03762094 | -1.19959353 | -3.69661517 |
| C | 0.53611464 | -2.65832649 | -3.22828732 |
| C | 0.74054511 | -0.30867633 | -4.29323515 |
| H | 1.41177052 | -2.77496235 | -3.87412339 |
| H | -0.22926274 | -3.35389273 | -3.59550790 |
| C | -0.34929468 | -2.93393942 | -0.89345044 |
| H | 1.32540764 | -4.03315202 | -1.74904235 |
| H | -0.07200045 | -3.10639102 | 0.15363076 |
| H | -1.05648603 | -3.72717486 | -1.16926817 |
| H | -1.96945888 | -1.61079079 | -1.58191354 |
| H | -1.21031412 | -1.09001977 | -0.07763069 |
| O | 0.20673838 | 0.49985634 | -5.03228178 |
| O | 2.08058518 | -0.48253844 | -4.25803290 |
| C | 2.85404023 | 0.37619709 | -5.11240040 |
| H | 2.66429296 | 1.42534871 | -4.87081876 |
| H | 2.60416622 | 0.19694612 | -6.16212844 |
| H | 3.89540781 | 0.11906338 | -4.91461705 |
| H | -0.49663003 | 2.64470112 | -0.59850235 |
| H | -0.52921916 | 1.11598143 | 0.31908943 |
| H | -1.71581013 | 0.85849746 | -1.90423482 |
| H | -0.26351252 | 1.42241984 | -2.72460327 |

Table B.78 90 degree enolate complex (swapped) with substrate K.

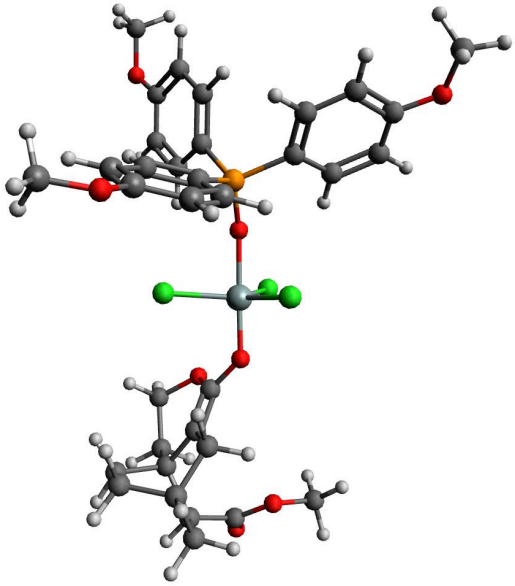


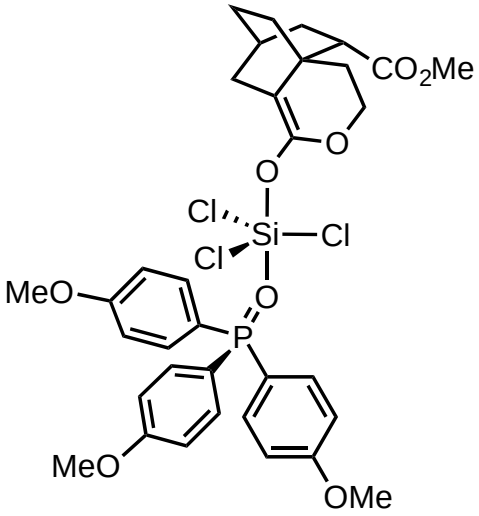

90° O-Si-O enolate free energy: -3931.96723395537

| | | | |
|---|---|---|---|
| C | -0.05554301 | -0.11932751 | -1.65703166 |
| C | 1.42709912 | -0.06229127 | -1.33610023 |
| C | -0.90266551 | 0.01733268 | -0.37682092 |
| C | 2.33760625 | -0.12347762 | -2.54734536 |
| O | 1.08361708 | -0.05468280 | 1.03843741 |
| C | -0.20095851 | -0.64821869 | 0.80343360 |
| C | 1.88138841 | -0.00499922 | -0.07180999 |
| O | 3.18418763 | 0.15870077 | 0.22299996 |
| H | 3.09591222 | -0.91005853 | -2.42580077 |
| C | -0.34333634 | -1.47331621 | -2.37138780 |
| C | -0.39820290 | 0.98777250 | -2.73398900 |
| C | 1.46431668 | -0.41401485 | -3.78415582 |
| P | 6.85536949 | 0.75470987 | 0.33113572 |
| O | 5.51980389 | -0.05480743 | 0.34176610 |
| C | 8.22213430 | -0.35879267 | -0.04061887 |
| C | 6.64000597 | 1.95183971 | -1.00578483 |
| C | 6.91801874 | 3.01896992 | 1.96795457 |
| C | 7.66591190 | 0.95164483 | 2.98993885 |
| C | 7.85906641 | 1.61348396 | 4.19978962 |
| C | 7.11049251 | 3.68512667 | 3.16845105 |
| C | 7.57745068 | 2.98556087 | 4.29503990 |
| H | 8.20722499 | 1.05017372 | 5.05766906 |
| H | 6.89392153 | 4.74453241 | 3.26406899 |
| O | 7.72338697 | 3.71984569 | 5.42529850 |
| C | 7.96581050 | -1.57033322 | -0.71192030 |
| C | 9.54475322 | -0.01755801 | 0.26826482 |
| C | 10.60370534 | -0.85570987 | -0.08752448 |
| C | 9.01029444 | -2.40794875 | -1.06883332 |
| H | 6.94407933 | -1.86245335 | -0.93126615 |
| H | 9.76453954 | 0.90144292 | 0.80533428 |
| C | 10.33714869 | -2.05594795 | -0.76301057 |
| H | 11.61610505 | -0.56957548 | 0.17387605 |
| O | 11.28662485 | -2.94270514 | -1.15675612 |
| H | 8.82377464 | -3.35047719 | -1.57401426 |
| C | 5.33568070 | 2.29077212 | -1.41640864 |
| C | 7.73502046 | 2.56803266 | -1.62498462 |
| H | 4.47960451 | 1.80051585 | -0.96098089 |
| C | 5.14422260 | 3.23444911 | -2.41606050 |
| C | 6.24516326 | 3.86016116 | -3.02422178 |
| C | 7.54853816 | 3.52044173 | -2.62816397 |
| H | 8.41427230 | 3.97804584 | -3.09316912 |
| H | 8.75039463 | 2.30637784 | -1.33863082 |
| H | 4.14460776 | 3.49261808 | -2.75161624 |
| O | 5.94731236 | 4.77202757 | -3.98588129 |
| C | 7.01056576 | 5.44892713 | -4.65138282 |

| | | | |
|---|---|---|---|
| H | 6.52950633 | 6.12403623 | -5.36026307 |
| H | 7.65118805 | 4.74265633 | -5.19426527 |
| H | 7.61470684 | 6.03000496 | -3.94323802 |
| C | 12.65416577 | -2.66592318 | -0.86680564 |
| H | 13.21597692 | -3.50830119 | -1.27235488 |
| H | 12.82359898 | -2.59911595 | 0.21505347 |
| H | 12.98184665 | -1.73833713 | -1.35285833 |
| C | 8.11578126 | 3.06381479 | 6.63052261 |
| H | 7.39631226 | 2.28328169 | 6.90507354 |
| H | 8.12475399 | 3.84057890 | 7.39609910 |
| H | 9.11888951 | 2.63012916 | 6.53565607 |
| C | 7.19514569 | 1.64093771 | 1.85963232 |
| H | 7.84916106 | -0.11646100 | 2.93920730 |
| H | 6.54206918 | 3.57004881 | 1.11160613 |
| Si | 4.21740115 | -0.78369032 | 1.26692529 |
| H | 2.88424907 | 0.81947873 | -2.69510853 |
| Cl | 5.82460446 | -1.99141803 | 2.33333736 |
| Cl | 3.72836528 | 0.24971965 | 3.03075554 |
| Cl | 3.26865284 | -2.61582259 | 0.73744807 |
| H | -1.45726683 | 0.86140283 | -2.98372015 |
| C | 0.48238180 | 0.75421752 | -4.00424900 |
| C | -0.32799343 | 2.39475339 | -2.16756448 |
| H | 1.03924146 | 1.66259826 | -4.25538830 |
| H | -0.16824248 | 0.53299658 | -4.86017826 |
| C | 0.66208205 | -1.70534129 | -3.53535357 |
| H | 2.09833901 | -0.52908252 | -4.67297463 |
| H | 1.35327458 | -2.52088199 | -3.28797726 |
| H | 0.13255231 | -2.00418428 | -4.44945893 |
| H | -1.37874604 | -1.46455411 | -2.74155794 |
| H | -0.27476555 | -2.28393415 | -1.63824582 |
| O | -1.28895961 | 2.99390608 | -1.71795436 |
| O | 0.91363084 | 2.93378346 | -2.18245865 |
| C | 1.03314113 | 4.23514264 | -1.58156362 |
| H | 0.78872672 | 4.18453790 | -0.51706437 |
| H | 0.36472583 | 4.94724261 | -2.07285277 |
| H | 2.07527730 | 4.52600556 | -1.71914513 |
| H | -1.89217004 | -0.43778975 | -0.52215226 |
| H | -1.07225895 | 1.06953543 | -0.12631518 |
| H | -0.75703247 | -0.50752752 | 1.73396513 |
| H | -0.05652956 | -1.72484408 | 0.63823915 |

Table B.79 180 degree enolate complex with substrate K.






180° O-Si-O enolate free energy: -3931.97416527427

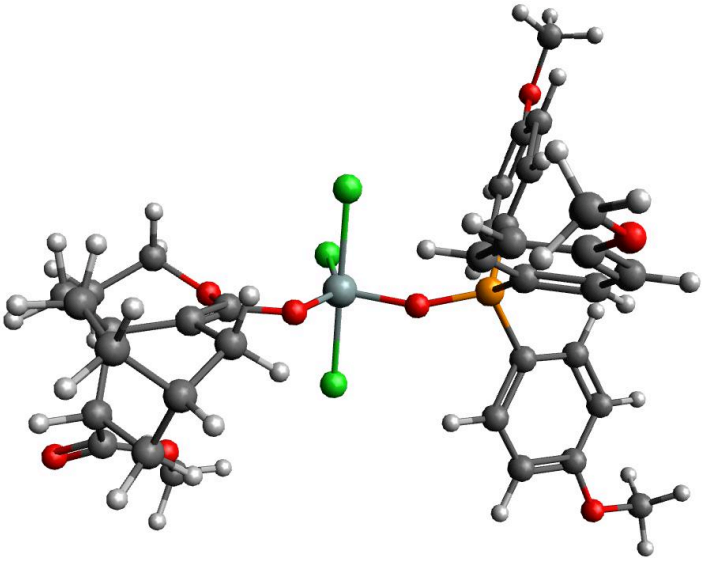
85

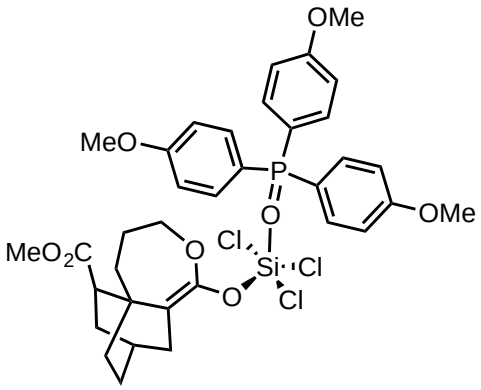
| | | | |
|---|---|---|---|
| C | -0.35887490 | -1.62627043 | -1.14656439 |
| C | 0.85611100 | -0.87592730 | -1.66450792 |
| C | -0.97437493 | -0.90023215 | 0.06448987 |
| C | 1.48323470 | -1.46733805 | -2.91039626 |
| O | 0.83849610 | 0.73404469 | 0.11666096 |
| H | -1.53390816 | -1.60783466 | 0.69231996 |
| H | -1.68571574 | -0.13205269 | -0.25592967 |
| C | 0.11130179 | -0.22515371 | 0.89750613 |
| H | 0.82879731 | -0.95590503 | 1.29796725 |
| H | -0.31462654 | 0.34320034 | 1.72847977 |
| C | 1.33093613 | 0.22268210 | -1.05467579 |
| Cl | 2.84529959 | 3.38732377 | -0.14471436 |
| H | 2.56486513 | -1.60802066 | -2.77673123 |
| C | 0.09358313 | -3.06752291 | -0.77126680 |
| C | -1.39331312 | -1.81820731 | -2.32860148 |
| C | 0.79708761 | -2.82027613 | -3.18609643 |
| P | 6.88142255 | 2.29484122 | -0.02562862 |
| Cl | 4.64550000 | 1.74014370 | -2.78108916 |
| C | 7.66171483 | 0.72351357 | -0.46823706 |
| C | 7.57163799 | 3.59108117 | -1.08085534 |
| C | 6.26069121 | 2.48592160 | 2.68493406 |
| C | 8.52421917 | 3.11190516 | 2.10445798 |
| C | 8.80376117 | 3.38728771 | 3.44401389 |
| C | 6.52911336 | 2.75589720 | 4.02025984 |
| C | 7.80061778 | 3.20850662 | 4.40941760 |

| | | | |
|---|---|---|---|
| H | 9.78971365 | 3.74521952 | 3.71737367 |
| H | 5.76343708 | 2.63207141 | 4.77996026 |
| O | 7.96060166 | 3.45149794 | 5.73731299 |
| C | 7.85629901 | 0.37238433 | -1.82096220 |
| C | 8.01252209 | -0.20270786 | 0.52381990 |
| C | 8.54678915 | -1.44842767 | 0.19229980 |
| C | 8.39108351 | -0.86034996 | -2.16044316 |
| H | 7.57062987 | 1.06041043 | -2.61020603 |
| H | 7.86418106 | 0.03759420 | 1.57224359 |
| C | 8.73591158 | -1.78261372 | -1.15632989 |
| H | 8.80237954 | -2.14251441 | 0.98459662 |
| O | 9.24184648 | -2.96471675 | -1.59149204 |
| H | 8.53755268 | -1.14049856 | -3.19901631 |
| C | 6.73928688 | 4.66137903 | -1.46407793 |
| C | 8.90928011 | 3.58826240 | -1.49505859 |
| H | 5.69364662 | 4.66291990 | -1.17077443 |
| C | 7.24109949 | 5.69865526 | -2.23580123 |
| C | 8.58642476 | 5.69124200 | -2.64358768 |
| C | 9.42429982 | 4.62994842 | -2.27040551 |
| H | 10.46167255 | 4.59574096 | -2.58321631 |
| H | 9.56375470 | 2.76065745 | -1.23368915 |
| H | 6.60571202 | 6.52157883 | -2.54833683 |
| O | 8.97863072 | 6.74787989 | -3.40279300 |
| C | 10.32197039 | 6.79757896 | -3.87428688 |
| H | 10.39343444 | 7.71470724 | -4.46058822 |
| H | 10.54982669 | 5.93520599 | -4.51331258 |
| H | 11.03364715 | 6.83958666 | -3.03981498 |
| C | 9.55986623 | -3.97362709 | -0.63554509 |
| H | 9.90624718 | -4.82901943 | -1.21701547 |
| H | 8.67445707 | -4.25787777 | -0.05398872 |
| H | 10.35822352 | -3.64213155 | 0.04044035 |
| C | 9.21297209 | 3.94505530 | 6.20335104 |
| H | 10.02092441 | 3.22940869 | 6.00503567 |
| H | 9.09578485 | 4.07230732 | 7.28041328 |
| H | 9.45238962 | 4.91208115 | 5.74366003 |
| C | 7.26056529 | 2.65717220 | 1.70893430 |
| H | 9.30759178 | 3.26923282 | 1.36797461 |
| H | 5.27185521 | 2.15000794 | 2.38955735 |
| Si | 3.74085588 | 1.61941523 | -0.86105043 |
| H | 1.35920813 | -0.80036478 | -3.77553152 |
| O | 2.32822175 | 0.95812273 | -1.57825466 |
| O | 5.33955331 | 2.32547005 | -0.13702925 |
| Cl | 4.06364590 | -0.04862401 | 0.44264552 |
| H | -2.22104059 | -2.41531145 | -1.93072178 |
| C | -0.69305930 | -2.58340143 | -3.49937263 |
| C | -2.04493274 | -0.50912484 | -2.74302012 |

| | | | |
|---|---|---|---|
| H | -0.78646132 | -2.01822663 | -4.43171124 |
| H | -1.19513529 | -3.54729276 | -3.65468093 |
| C | 0.90986745 | -3.70719499 | -1.93021145 |
| H | 1.27369878 | -3.31590197 | -4.04189122 |
| H | 1.96603699 | -3.80472107 | -1.64791769 |
| H | 0.54385724 | -4.71962508 | -2.14634761 |
| H | -0.79767239 | -3.66919286 | -0.53829605 |
| H | 0.69366914 | -3.02388195 | 0.14470186 |
| O | -3.11743685 | -0.11601995 | -2.31666859 |
| O | -1.30612427 | 0.20373804 | -3.61860629 |
| C | -1.81728601 | 1.49831581 | -3.97963080 |
| H | -1.91140612 | 2.12880464 | -3.09158540 |
| H | -2.79435697 | 1.40193416 | -4.46157167 |
| H | -1.08298080 | 1.91604381 | -4.66915206 |

Table B.80 120 degree enolate complex with substrate 7-K.






120° O-Si-O enolate free energy: -3971.26967844405

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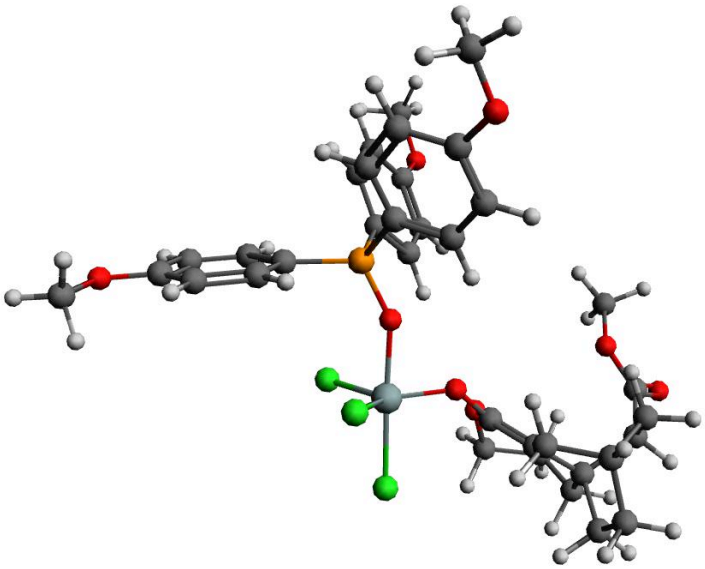
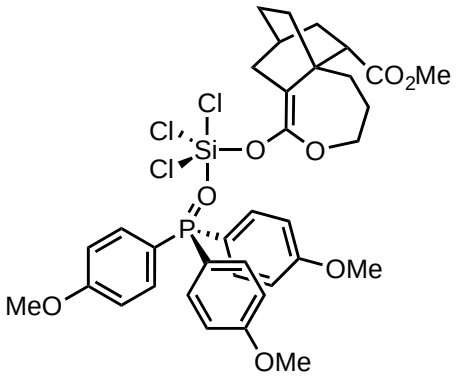
| | | | |
|---|---|---|---|
| C | -0.10689185 | -1.44056950 | -1.01939773 |
| C | 1.32355844 | -0.92671518 | -0.84842593 |
| C | -1.18172573 | -1.03198031 | 0.01874108 |
| C | 2.32663547 | -1.71357221 | -1.69385718 |
| O | 1.09330747 | 1.16180911 | 0.44241351 |
| C | 0.01673651 | 0.80604214 | 1.31587695 |
| C | 1.75699194 | 0.21361808 | -0.27685392 |
| O | 3.04071160 | 0.61705568 | -0.44747386 |
| H | 2.91865682 | -2.41175677 | -1.07930684 |
| C | -0.05527741 | -3.00524337 | -0.95060952 |

| | | | |
|---|---|---|---|
| C | -0.55126806 | -1.12153557 | -2.50945386 |
| C | 1.56698453 | -2.49908190 | -2.77912240 |
| P | 6.93984891 | 2.15812740 | -0.09185868 |
| O | 5.40395158 | 1.92012152 | -0.24821079 |
| C | 7.75102098 | 0.59293323 | -0.46836578 |
| C | 7.39377870 | 3.40719980 | -1.30818226 |
| C | 7.03669152 | 4.01850985 | 1.97162270 |
| C | 8.13038377 | 1.90166249 | 2.42150934 |
| C | 8.46683709 | 2.33905489 | 3.70230443 |
| C | 7.36741408 | 4.46059962 | 3.24104406 |
| C | 8.08343411 | 3.62315986 | 4.11687122 |
| H | 9.01057933 | 1.67340136 | 4.36256269 |
| H | 7.06711278 | 5.44397780 | 3.58857913 |
| O | 8.35329302 | 4.14784243 | 5.33727466 |
| C | 9.09678991 | 0.56117563 | -0.88400751 |
| C | 7.04573372 | -0.61018857 | -0.33431655 |
| C | 7.66852631 | -1.83047978 | -0.60384655 |
| C | 9.72334392 | -0.64766158 | -1.14502758 |
| H | 9.65535633 | 1.48459449 | -1.01234124 |
| H | 6.01013443 | -0.60073170 | -0.00912217 |
| C | 9.01159119 | -1.85372341 | -1.00618914 |
| H | 7.09700473 | -2.74508401 | -0.49617180 |
| O | 9.71273399 | -2.98159466 | -1.28669492 |
| H | 10.75854343 | -0.68793417 | -1.46958008 |
| C | 6.62825408 | 3.52414118 | -2.48660381 |
| C | 8.51580079 | 4.22880428 | -1.13633593 |
| H | 5.72938785 | 2.92837329 | -2.61105386 |
| C | 6.99159595 | 4.43439203 | -3.46629931 |
| C | 8.12403733 | 5.24974431 | -3.29292619 |
| C | 8.88742238 | 5.14797945 | -2.11970775 |
| H | 9.75319605 | 5.77937006 | -1.95588307 |
| H | 9.10493876 | 4.17271329 | -0.22479168 |
| H | 6.40012845 | 4.54738942 | -4.36954926 |
| O | 8.38872867 | 6.10896031 | -4.30943780 |
| C | 9.47951542 | 7.01758853 | -4.18389301 |
| H | 9.47103770 | 7.61245692 | -5.09812697 |
| H | 10.43458482 | 6.48353650 | -4.10254941 |
| H | 9.34562276 | 7.67507743 | -3.31601256 |
| C | 9.05614216 | -4.24522619 | -1.19675544 |
| H | 9.81052818 | -4.98566943 | -1.46647735 |
| H | 8.21526814 | -4.30337597 | -1.89875787 |
| H | 8.70229902 | -4.43684663 | -0.17634649 |
| C | 9.00804007 | 3.33697563 | 6.31078938 |
| H | 8.41560866 | 2.44298117 | 6.53971049 |
| H | 9.09010429 | 3.95988074 | 7.20218565 |
| H | 10.01064328 | 3.04516732 | 5.97435874 |

| | | | |
|---|---|---|---|
| C | 7.42101724 | 2.73031010 | 1.54197845 |
| H | 8.41675620 | 0.89999233 | 2.11590753 |
| H | 6.45941003 | 4.66520893 | 1.31663158 |
| Si | 3.78358386 | 1.90684512 | 0.34347743 |
| H | 3.04059594 | -1.02479948 | -2.15796505 |
| Cl | 4.39292844 | 0.49967235 | 2.01857231 |
| Cl | 3.19996343 | 3.30182597 | -1.30168628 |
| Cl | 3.30463259 | 3.38705425 | 1.78815746 |
| H | -1.44664248 | -1.72577664 | -2.69852180 |
| C | 0.59032834 | -1.54128709 | -3.48547085 |
| C | -1.01673322 | 0.30981769 | -2.72028087 |
| H | 1.13545397 | -0.65462217 | -3.82227506 |
| H | 0.15465875 | -2.01991458 | -4.37256100 |
| C | 0.76492644 | -3.62410860 | -2.10947455 |
| H | 2.27485536 | -2.91261108 | -3.50962527 |
| H | 1.43818865 | -4.40391329 | -1.73061819 |
| H | 0.10625837 | -4.10475053 | -2.84600958 |
| H | -1.08295897 | -3.39042912 | -0.95341999 |
| H | 0.38089558 | -3.27355149 | 0.01911329 |
| O | -2.18804629 | 0.64914387 | -2.75701393 |
| O | 0.00526977 | 1.17662997 | -2.84382697 |
| C | -0.32206955 | 2.57202181 | -2.96940346 |
| H | -0.99777697 | 2.87827039 | -2.16706963 |
| H | -0.79962367 | 2.76088243 | -3.93588974 |
| H | 0.63055868 | 3.09491435 | -2.88702908 |
| C | -1.23969645 | 0.39861309 | 0.56369120 |
| H | -1.45058553 | 1.13865382 | -0.21589890 |
| H | -2.08296621 | 0.45091990 | 1.26805054 |
| H | -0.14910071 | 1.71441311 | 1.90200198 |
| H | 0.35784446 | 0.00774108 | 1.99144182 |
| H | -1.05898624 | -1.69488276 | 0.88798892 |
| H | -2.15954816 | -1.27996010 | -0.41487227 |

Table B.81 90 degree enolate complex with substrate 7-K.






90° O-Si-O enolate free energy: -3971.27843341805

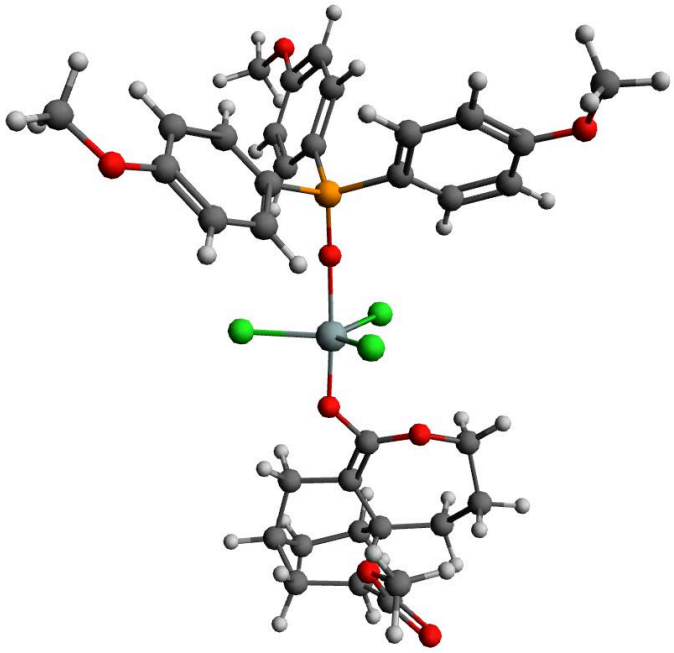
88

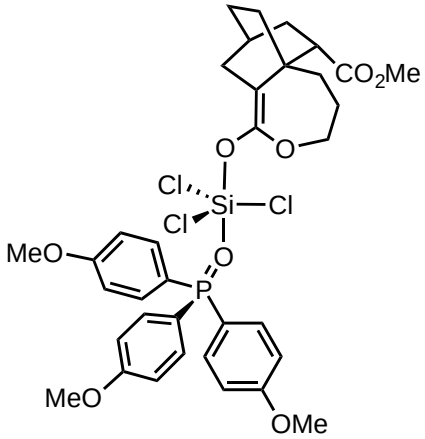
| | | | |
|---|---|---|---|
| C | -0.10735466 | -0.78218654 | -1.78378553 |
| C | 1.20653516 | -0.65109398 | -1.01469991 |
| C | -1.21740131 | 0.27365872 | -1.56041671 |
| C | 2.02839160 | -1.94312644 | -1.04794937 |
| O | 1.36630403 | 1.72470300 | -0.35288696 |
| C | -0.01858143 | 2.03943561 | -0.18217633 |
| C | 1.77659915 | 0.42866553 | -0.44911440 |
| O | 3.05895865 | 0.35102716 | 0.01248126 |
| H | 1.99181415 | -2.46770775 | -0.08045722 |
| C | -0.75433543 | -2.14625917 | -1.35843634 |
| C | 0.24408585 | -0.97331129 | -3.32016823 |
| C | 1.49629443 | -2.85664825 | -2.16707798 |
| P | 6.63517507 | 1.60525365 | 0.59125095 |
| O | 5.23946799 | 0.95352470 | 0.63298668 |
| C | 7.68503866 | 0.50509195 | -0.39269880 |
| C | 6.48608659 | 3.19965432 | -0.25574128 |
| C | 7.42353069 | 3.10683688 | 2.83583741 |
| C | 7.95039582 | 0.74515874 | 2.87925452 |
| C | 8.47797087 | 0.87672649 | 4.16274303 |
| C | 7.95090667 | 3.25028134 | 4.11020280 |
| C | 8.47847547 | 2.13511775 | 4.78451351 |
| H | 8.86612697 | -0.00047075 | 4.66723439 |
| H | 7.94607744 | 4.21200855 | 4.61397694 |
| O | 8.96094013 | 2.37368630 | 6.03032786 |
| C | 7.06900814 | -0.40533489 | -1.27337000 |

| | | | |
|---|---|---|---|
| C | 9.08297112 | 0.57445020 | -0.35815177 |
| C | 9.86498775 | -0.23824574 | -1.18253629 |
| C | 7.83708147 | -1.21597520 | -2.09691744 |
| H | 5.98584371 | -0.47987831 | -1.29773270 |
| H | 9.58403115 | 1.25324809 | 0.32727622 |
| C | 9.23969795 | -1.13694185 | -2.05895436 |
| H | 10.94525697 | -0.16777302 | -1.12676374 |
| O | 9.90193627 | -1.97273544 | -2.90190753 |
| H | 7.37316839 | -1.92495231 | -2.77594136 |
| C | 5.22913604 | 3.60508519 | -0.74213567 |
| C | 7.60071943 | 4.01547408 | -0.48766958 |
| H | 4.35599857 | 2.98315223 | -0.57358230 |
| C | 5.09919114 | 4.79905919 | -1.43904201 |
| C | 6.22142310 | 5.61151442 | -1.66821058 |
| C | 7.48025129 | 5.21678710 | -1.18752172 |
| H | 8.36126192 | 5.82760639 | -1.34905067 |
| H | 8.58161716 | 3.72243407 | -0.12055071 |
| H | 4.13267774 | 5.12531690 | -1.81106738 |
| O | 5.99114003 | 6.75654609 | -2.36407338 |
| C | 7.08621128 | 7.61908089 | -2.65618832 |
| H | 6.66172319 | 8.44984639 | -3.22151434 |
| H | 7.84092090 | 7.10788805 | -3.26721442 |
| H | 7.54832397 | 8.00030945 | -1.73682447 |
| C | 11.32585355 | -1.94847559 | -2.92022174 |
| H | 11.62115431 | -2.68612312 | -3.66754091 |
| H | 11.74028442 | -2.22855145 | -1.94344206 |
| H | 11.70118829 | -0.95945236 | -3.21154207 |
| C | 9.44903812 | 1.27978400 | 6.80478033 |
| H | 8.66484725 | 0.53026936 | 6.96503986 |
| H | 9.74740327 | 1.70987003 | 7.76174571 |
| H | 10.31789227 | 0.81168800 | 6.32527545 |
| C | 7.42433538 | 1.85217428 | 2.19615053 |
| H | 7.93228466 | -0.23823644 | 2.41901757 |
| H | 6.99138539 | 3.96964859 | 2.33914541 |
| Si | 3.66709266 | 0.52736829 | 1.56959349 |
| H | 3.08239032 | -1.70600489 | -1.22993187 |
| Cl | 4.72520505 | -1.10011656 | 2.42539133 |
| Cl | 3.81501738 | 2.39799695 | 2.56735452 |
| Cl | 1.79708224 | 0.00937502 | 2.59004447 |
| H | -0.67189206 | -1.34888779 | -3.79172049 |
| C | 1.38259926 | -2.03001074 | -3.46027152 |
| C | 0.52578313 | 0.31622132 | -4.06952645 |
| H | 2.33671562 | -1.53092722 | -3.65746930 |
| H | 1.17028797 | -2.68116752 | -4.31866575 |
| C | 0.10337240 | -3.36637880 | -1.77221888 |
| H | 2.18468921 | -3.69742063 | -2.32288643 |

| | | | |
|---|---|---|---|
| H | 0.17921829 | -4.08140219 | -0.94328820 |
| H | -0.35372797 | -3.90299166 | -2.61500812 |
| H | -1.75918723 | -2.21143135 | -1.79644659 |
| H | -0.88548507 | -2.11871514 | -0.27039737 |
| O | -0.29033273 | 0.89345874 | -4.76726056 |
| O | 1.78256439 | 0.77981729 | -3.88923092 |
| C | 2.10774375 | 2.01287511 | -4.55163041 |
| H | 1.45397152 | 2.81802196 | -4.20474183 |
| H | 1.99996428 | 1.90560120 | -5.63494320 |
| H | 3.14486992 | 2.21792021 | -4.28342892 |
| C | -0.85336315 | 1.75443887 | -1.42160938 |
| H | -0.33625739 | 2.14401396 | -2.30535458 |
| H | -1.79020769 | 2.32375950 | -1.33789420 |
| H | -1.74957775 | -0.00517922 | -0.63963784 |
| H | -1.94475095 | 0.15894263 | -2.37493735 |
| H | -0.01291150 | 3.10806251 | 0.05203648 |
| H | -0.39926678 | 1.49078234 | 0.69018175 |

Table B.82 180 degree enolate complex with substrate 7-K.






180° O-Si-O enolate free energy: -3971.27471245431

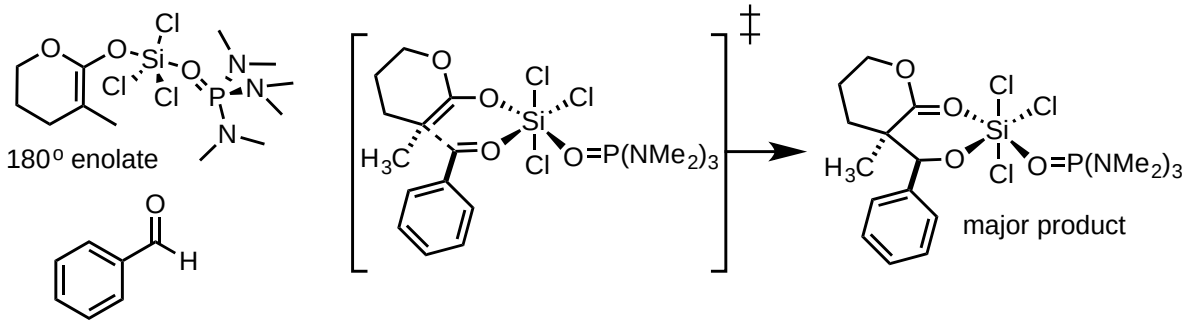
88

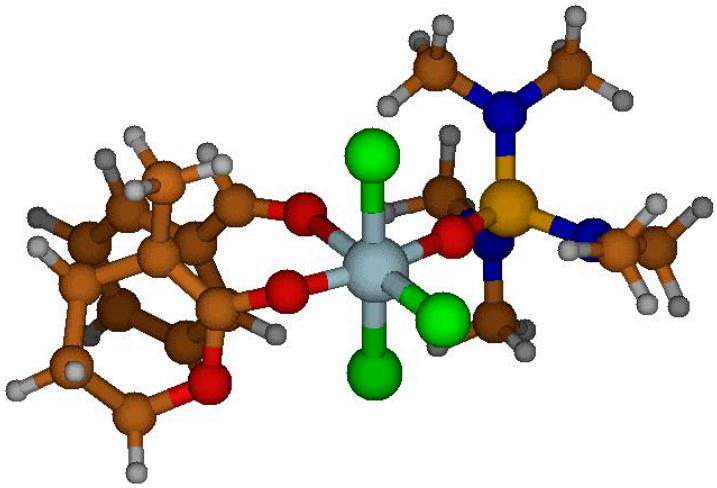
| | | | |
|---|---|---|---|
| C | -0.79408479 | -0.96288582 | -1.48081304 |
| C | 0.70190475 | -1.00531123 | -1.16978661 |
| C | -1.53623889 | 0.39426041 | -1.40614901 |
| C | 1.18499686 | -2.42551349 | -0.86641901 |

| | | | |
|---|---|---|---|
| O | 1.51443667 | 1.25236848 | -1.71944425 |
| C | 0.40277550 | 2.03592119 | -1.28623857 |
| C | 1.64195324 | -0.04962671 | -1.33308623 |
| O | 2.94842758 | -0.38733586 | -1.21560880 |
| H | 1.33307322 | -2.58431059 | 0.21426901 |
| C | -1.51827147 | -1.86697082 | -0.42280673 |
| C | -1.01983101 | -1.71249761 | -2.86023671 |
| C | 0.15050573 | -3.43526525 | -1.40191646 |
| P | 7.20577165 | 1.93272191 | 0.30276587 |
| O | 5.83932132 | 1.24473774 | 0.16071111 |
| C | 8.51525318 | 1.14219440 | -0.66413088 |
| C | 7.08691352 | 3.66761490 | -0.18828027 |
| C | 8.48446099 | 2.80609424 | 2.66333686 |
| C | 7.13884312 | 0.80124868 | 2.83273846 |
| C | 7.45999456 | 0.69247198 | 4.18714593 |
| C | 8.81114429 | 2.70541154 | 4.00871645 |
| C | 8.30127022 | 1.64587453 | 4.77943553 |
| H | 7.04405789 | -0.12533929 | 4.76440893 |
| H | 9.44831379 | 3.44120028 | 4.48983090 |
| O | 8.67519442 | 1.63658121 | 6.08607563 |
| C | 8.33301972 | 0.94260345 | -2.04916178 |
| C | 9.70569250 | 0.70613881 | -0.06962486 |
| C | 10.70793482 | 0.09372565 | -0.82698263 |
| C | 9.32071662 | 0.33579432 | -2.80780806 |
| H | 7.40456887 | 1.24509528 | -2.52441739 |
| H | 9.86210790 | 0.83359563 | 0.99723961 |
| C | 10.51629599 | -0.09331011 | -2.20268911 |
| H | 11.61616833 | -0.23485597 | -0.33491205 |
| O | 11.41743625 | -0.67884922 | -3.03327279 |
| H | 9.18491630 | 0.16724975 | -3.87172287 |
| C | 5.88349750 | 4.35713808 | 0.06384354 |
| C | 8.15624796 | 4.35536580 | -0.77245023 |
| H | 5.03779623 | 3.82939793 | 0.49626233 |
| C | 5.76415671 | 5.69967549 | -0.25817933 |
| C | 6.84446654 | 6.38593294 | -0.84218489 |
| C | 8.04593968 | 5.70983427 | -1.09923778 |
| H | 8.88855243 | 6.21462231 | -1.55825346 |
| H | 9.08575925 | 3.83693084 | -0.99225289 |
| H | 4.83890056 | 6.23893782 | -0.07998148 |
| O | 6.62332581 | 7.69618713 | -1.12570807 |
| C | 7.66184492 | 8.45426717 | -1.73900264 |
| H | 7.25197691 | 9.45571937 | -1.87679250 |
| H | 7.93605652 | 8.03286336 | -2.71413535 |
| H | 8.54805551 | 8.50639362 | -1.09395395 |
| C | 12.63089671 | -1.18811489 | -2.48678390 |
| H | 13.17120273 | -1.62441192 | -3.32791541 |

| | | | |
|---|---|---|---|
| H | 12.43091536 | -1.96324658 | -1.73662089 |
| H | 13.23281267 | -0.38624029 | -2.04103789 |
| C | 8.18574537 | 0.60085437 | 6.93494499 |
| H | 7.09070617 | 0.62292221 | 6.99489721 |
| H | 8.60953890 | 0.80406426 | 7.91932041 |
| H | 8.51865992 | -0.38516559 | 6.58742136 |
| C | 7.64951524 | 1.84975611 | 2.05618935 |
| H | 6.47121890 | 0.07256640 | 2.38247249 |
| H | 8.87137196 | 3.64212992 | 2.08672329 |
| Si | 4.31245933 | 0.43485268 | -0.60307004 |
| H | 2.15937022 | -2.59227406 | -1.33625724 |
| Cl | 3.29088461 | 1.30375211 | 1.05886699 |
| Cl | 4.68373171 | 1.56071912 | -2.36569406 |
| Cl | 5.34342682 | -1.40260632 | -0.39433983 |
| H | -2.09395540 | -1.92318025 | -2.92005178 |
| C | -0.21466948 | -3.05050489 | -2.84687185 |
| C | -0.74828170 | -0.86255997 | -4.08861344 |
| H | 0.70207042 | -2.94284726 | -3.43480658 |
| H | -0.81498843 | -3.84048163 | -3.31743699 |
| C | -1.11238858 | -3.35588073 | -0.53248157 |
| H | 0.57099872 | -4.44904502 | -1.38373656 |
| H | -0.92074121 | -3.77637949 | 0.46308733 |
| H | -1.91818356 | -3.95584472 | -0.97791449 |
| H | -2.60306675 | -1.75000263 | -0.54322868 |
| H | -1.26586077 | -1.47275497 | 0.56898844 |
| O | -1.61605068 | -0.30973231 | -4.74400453 |
| O | 0.56335835 | -0.76439159 | -4.38728274 |
| C | 0.90835949 | 0.06878577 | -5.50559033 |
| H | 0.56757469 | 1.09405572 | -5.33711020 |
| H | 0.45408375 | -0.31631679 | -6.42322448 |
| H | 1.99652953 | 0.03449770 | -5.56425487 |
| C | -0.89681628 | 1.66041110 | -1.98037796 |
| H | -0.72002529 | 1.58759644 | -3.05837112 |
| H | -1.60832490 | 2.48753680 | -1.84072246 |
| H | -1.72898298 | 0.59401849 | -0.34166737 |
| H | -2.52107032 | 0.25414579 | -1.87204358 |
| H | 0.69487691 | 3.06159835 | -1.53299970 |
| H | 0.31042765 | 1.95162001 | -0.19338077 |

Table B.83 HMPA aldol TS (major product).



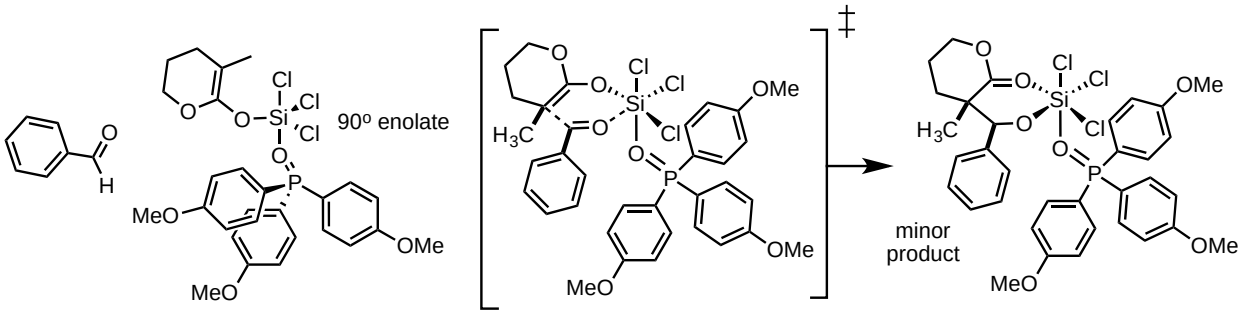
TS Free Energy: -3220.691301

64

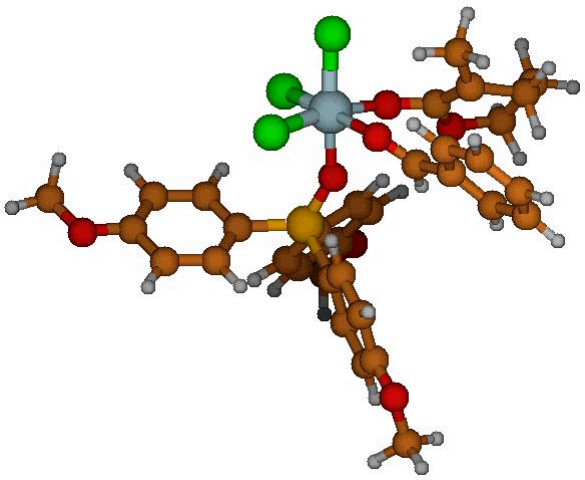
C -0.936653 -2.840184 2.984710
C -1.589615 -2.596114 4.200763
C -1.786100 -1.282394 4.637210
C -0.484821 -1.780067 2.201067
H -1.943914 -3.427972 4.804670
H -0.782026 -3.862616 2.648129
C -0.673846 -0.455511 2.638179
H 0.028793 -1.954025 1.260061
C -1.324590 -0.217541 3.861423
H -2.293739 -1.088871 5.578850
C -0.266795 0.696023 1.812817
H -1.476094 0.806384 4.197346
O -0.059331 0.618343 0.578547
H -0.441533 1.683870 2.264612
C 2.134245 0.793347 4.367301
C 2.025250 1.313832 2.947255
C 3.384846 -0.087454 4.498723
C 1.868033 2.805456 2.778115

O 3.083730 -0.688519 2.121486
H 3.459234 -0.543368 5.494368
H 4.291344 0.509279 4.334624
C 3.289866 -1.192709 3.459025
H 2.453679 -1.864904 3.687739
H 4.205842 -1.786673 3.393657
C 2.541788 0.535685 1.935201
O 2.590199 0.928172 0.685526
H 1.765988 3.105473 1.734763
H 1.256810 0.183945 4.636223
H 2.152875 1.632682 5.073510
H 1.001764 3.182880 3.340486
Si 1.700315 0.740673 -0.801368
O 0.439757 0.492048 -2.057676
Cl 3.376923 0.866282 -2.125479
Cl 1.261108 2.896870 -0.868585
H 2.754463 3.309756 3.194435
Cl 1.766464 -1.484802 -0.645460
P -0.785970 0.182199 -2.915788
N -0.254629 -0.153684 -4.452178
N -1.802243 1.498625 -2.887491
N -1.655305 -1.170844 -2.482843
C -2.049876 2.291606 -1.676966
H -1.907284 3.354139 -1.903555
H -1.350731 2.020259 -0.887778
H -3.080578 2.140026 -1.321837
C -2.741469 1.760105 -3.975142
H -2.406549 1.294554 -4.903811
H -2.798806 2.842580 -4.141353
H -3.753328 1.393908 -3.742887
C -2.797419 -1.091356 -1.566243
H -2.481903 -1.205444 -0.519846
H -3.499539 -1.896928 -1.811712
H -3.318714 -0.139591 -1.678011
C -1.016454 -2.496357 -2.497328
H -1.714495 -3.226204 -2.929000
H -0.742971 -2.804185 -1.482729
H -0.103112 -2.475477 -3.091977
C 0.921940 0.526565 -5.011519
H 1.542371 -0.211349 -5.532816
H 1.529829 0.974074 -4.224890
H 0.620173 1.302969 -5.728540
C -1.020587 -0.915698 -5.437262
H -1.911533 -1.351092 -4.983545
H -0.400268 -1.727202 -5.840060
H -1.326494 -0.274286 -6.276949

Table B.84 4-OMe-TPPO aldol TS (minor product, 90 degree enolate).




TS Free Energy: -3855.498036



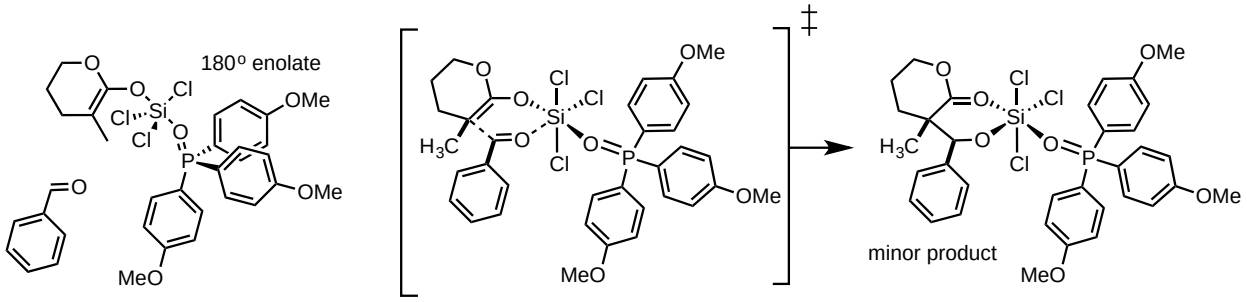
82

C 2.402487 -4.834711 1.493685
C 2.682568 -4.945563 2.859659
C 2.726663 -3.801733 3.667993
C 2.166520 -3.577402 0.937106
H 2.865785 -5.924016 3.296882
H 2.368246 -5.723327 0.868953
C 2.212034 -2.428330 1.741957
H 1.948156 -3.477588 -0.124387
C 2.492985 -2.545405 3.114172
H 2.944177 -3.895361 4.728782
C 1.946165 -1.111430 1.135276
H 2.521776 -1.645618 3.721660
H 1.689490 -1.116802 0.062128
O 1.946470 -0.058805 1.766623
C 5.487421 -1.384034 -0.841659
C 4.689092 -0.394127 -0.010010
C 5.946262 -0.701261 -2.134946
C 5.084385 -0.248041 1.435760
O 3.719062 0.395743 -2.064896
H 6.532299 -1.370017 -2.779785

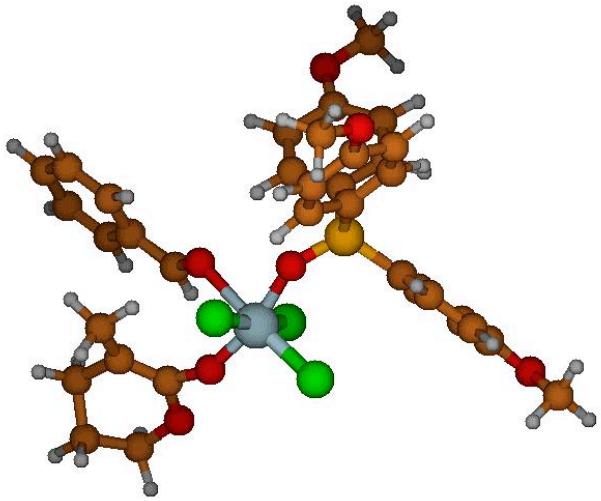
H 6.574126 0.164462 -1.891127
C 4.702256 -0.259889 -2.893712
H 4.204522 -1.130725 -3.341231
H 4.940087 0.448504 -3.695667
C 3.873585 0.450128 -0.691166
O 3.073003 1.396290 -0.239505
H 4.378017 0.338175 2.021104
H 4.881832 -2.266811 -1.110143
H 6.338176 -1.760276 -0.262222
H 5.187559 -1.235822 1.907179
Si 2.042852 2.272764 0.768735
O 0.702100 1.626513 -0.373722
Cl 0.550953 2.491118 2.298515
Cl 2.004625 4.163147 -0.281288
H 6.061785 0.252055 1.522475
Cl 3.681549 2.905392 2.050647
P -0.670028 1.822355 -1.060046
C -1.765600 3.087900 -0.366484
C -1.528099 0.228516 -0.929286
C -0.401129 2.216200 -2.802605
C -1.462850 4.447475 -0.537852
C -1.403446 2.802438 -3.586274
C -2.256820 -0.320691 -1.988824
C 0.831339 1.883412 -3.399682
H -2.351743 3.088406 -3.138706
C -1.200960 3.048325 -4.946340
C -2.910040 2.741717 0.378148
H -0.577064 4.742050 -1.089674
C -2.264655 5.439735 0.023505
C -1.467066 -0.472956 0.291992
H -2.304836 0.194105 -2.944252
C -2.921319 -1.543013 -1.849329
C -3.395780 5.079066 0.770860
H -1.989741 6.478872 -0.115990
C -3.716942 3.722088 0.937654
H -3.173544 1.699827 0.527409
C 1.038967 2.126999 -4.750152
H 1.631858 1.451166 -2.805755
C -2.857515 -2.229194 -0.628695
O -4.238937 5.963799 1.364413
H -4.596676 3.460202 1.517570
C 0.026567 2.706795 -5.532924
H -1.992078 3.510701 -5.525526
H -3.470849 -1.945618 -2.692524
O 0.331912 2.904855 -6.843904
H 1.988813 1.888628 -5.218880

C -2.124924 -1.685759 0.441786
H -0.898801 -0.061415 1.122004
H -2.082760 -2.234126 1.378075
O -3.464404 -3.421857 -0.384219
C -3.937189 7.355366 1.293190
C -0.640541 3.503051 -7.695036
C -4.228719 -4.029551 -1.421036
H -0.171279 3.567733 -8.677768
H -0.905765 4.509967 -7.348808
H -1.544608 2.884026 -7.760338
H -4.620416 -4.953952 -0.994264
H -3.601593 -4.264006 -2.290538
H -5.062315 -3.385532 -1.728549
H -4.726567 7.855682 1.855860
H -3.945528 7.709841 0.254853
H -2.964432 7.571035 1.751474

Table B.85 4-OMe-TPPO aldol TS (minor product, 180 degree enolate).




TS Free Energy: -3855.503414



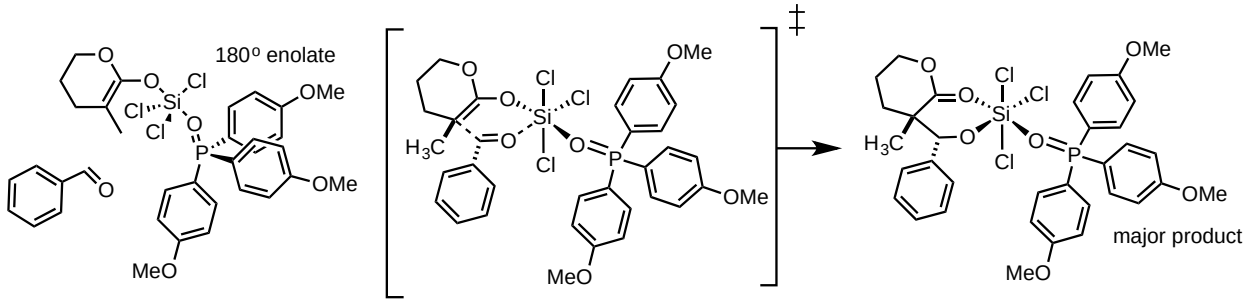
82

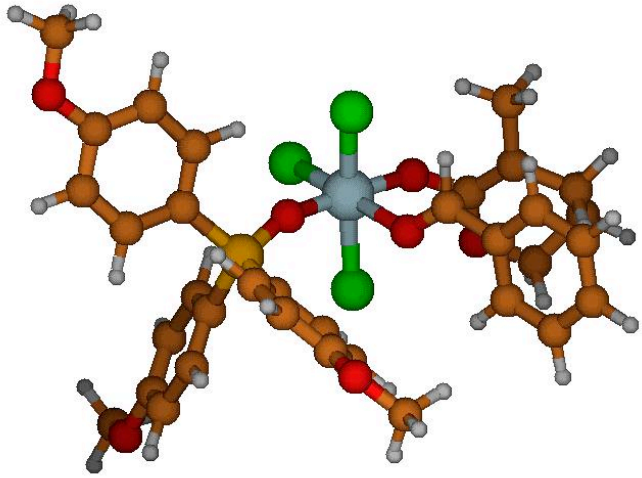
C 3.192272 -4.484783 2.425533
C 2.729404 -4.118616 3.693807

C 2.141009 -2.862798 3.895491
C 3.068828 -3.592856 1.360115
H 2.827326 -4.810521 4.526543
H 3.648323 -5.458994 2.270877
C 2.478552 -2.334210 1.555778
H 3.426804 -3.866225 0.369802
C 2.014432 -1.972083 2.832193
H 1.786167 -2.582231 4.883743
C 2.345591 -1.422289 0.408600
H 1.564177 -0.993242 2.967758
H 2.734117 -1.783804 -0.555247
O 1.746175 -0.344880 0.461776
C 6.358191 -0.971398 0.619282
C 5.105657 -0.120935 0.485942
C 7.389335 -0.543754 -0.429757
C 4.579750 0.494203 1.757177
O 5.443991 -0.109921 -1.898620
H 8.301655 -1.153781 -0.389944
H 7.678262 0.501406 -0.260858
C 6.752630 -0.698593 -1.803673
H 6.645781 -1.762953 -2.055080
H 7.345384 -0.220333 -2.590795
C 4.750482 0.260308 -0.773056
O 3.720025 0.995668 -1.160264
H 3.586520 0.927100 1.652016
H 6.133688 -2.041929 0.474374
H 6.762876 -0.880937 1.634518
H 4.549445 -0.253573 2.561671
Si 2.090120 1.452672 -1.288260
O 0.322728 1.619141 -0.979266
Cl 2.342680 2.795571 0.440166
Cl 2.272865 2.922072 -2.811695
H 5.247397 1.301377 2.099980
Cl 1.711847 -0.284943 -2.615352
P -1.095645 1.686804 -1.623323
C -1.982500 2.918215 -0.635632
C -1.914790 0.083362 -1.457218
C -1.156731 2.189848 -3.352726
C -1.331099 3.548761 0.431292
C -1.256416 3.547534 -3.689493
C -3.085284 -0.216098 -2.165295
C -1.012769 1.241350 -4.386417
H -1.345275 4.298185 -2.910447
C -1.229027 3.961456 -5.020123
C -3.327541 3.237455 -0.903748
H -0.291476 3.315777 0.643613

C -2.002884 4.488281 1.218560
C -1.420118 -0.852130 -0.529679
H -3.481384 0.481631 -2.898218
C -3.759495 -1.422290 -1.963834
C -3.339624 4.801158 0.941940
H -1.469280 4.963031 2.033910
C -4.000499 4.168466 -0.127643
H -3.852267 2.763215 -1.728826
C -0.989708 1.642689 -5.712045
H -0.892126 0.189926 -4.149023
C -3.257614 -2.347346 -1.036575
O -4.083533 5.698380 1.642942
H -5.036432 4.424759 -0.327057
C -1.094918 3.006093 -6.038525
H -1.300498 5.018594 -5.247364
H -4.659208 -1.627235 -2.532728
O -1.055997 3.298437 -7.363785
H -0.869310 0.921032 -6.513761
C -2.083665 -2.053521 -0.322949
H -0.505038 -0.639299 0.012959
H -1.705644 -2.785866 0.384195
O -3.831439 -3.550737 -0.765549
C -3.479762 6.380288 2.739506
C -1.089874 4.664402 -7.770722
C -5.023737 -3.915669 -1.453887
H -1.023789 4.647183 -8.859395
H -0.238176 5.219558 -7.359182
H -2.028653 5.144520 -7.467659
H -5.287290 -4.906065 -1.079894
H -4.857395 -3.966029 -2.537489
H -5.837843 -3.212972 -1.235804
H -4.252118 7.041356 3.135097
H -2.619511 6.975843 2.410118
H -3.164532 5.675036 3.518522

Table B.86 4-OMe-TPPO aldol TS (major product, 180 degree enolate).





TS Free Energy: -3855.505974

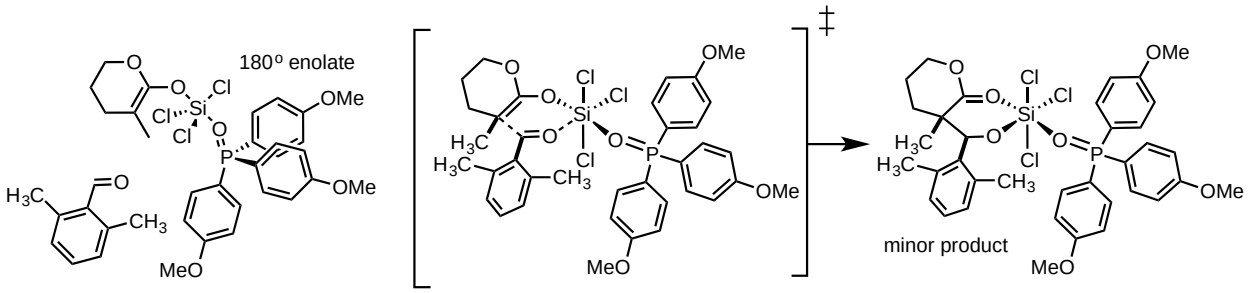
82

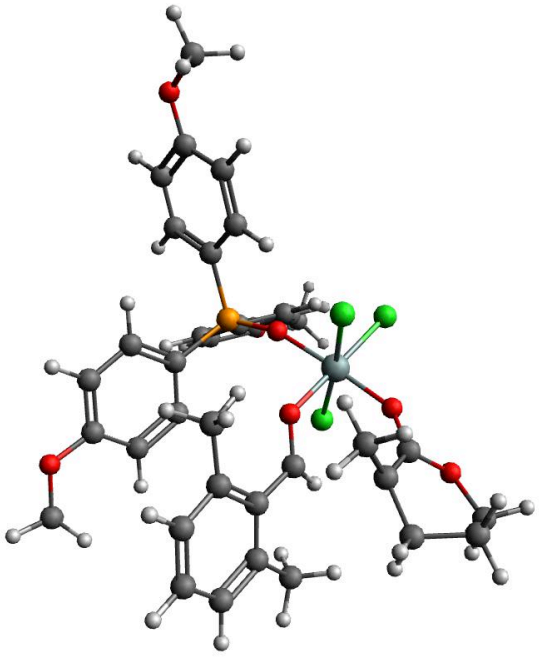
C 1.386823 -5.553786 0.756879
C 1.450382 -6.223584 1.987340
C 1.491115 -5.499918 3.183080
C 1.344344 -4.162315 0.721986
H 1.471395 -7.310307 2.011433
H 1.372108 -6.122436 -0.169142
C 1.378332 -3.430841 1.921824
H 1.291913 -3.620173 -0.217536
C 1.464613 -4.105061 3.148656
H 1.546052 -6.020671 4.135336
C 1.285593 -1.956110 1.910457
H 1.503415 -3.531792 4.073207
O 1.027136 -1.302981 0.910109
H 1.415185 -1.455250 2.887346
C 5.371256 -2.428392 1.149759
C 4.498130 -1.216299 1.428343
C 6.366623 -2.093074 0.033672
C 4.442783 -0.720600 2.852702
O 4.607781 -0.625824 -0.907214
H 6.990855 -2.954887 -0.238937
H 7.034657 -1.282691 0.352595
C 5.563022 -1.662417 -1.188000
H 5.009233 -2.519994 -1.595780
H 6.199582 -1.258064 -1.981939
C 4.182286 -0.422178 0.377332
O 3.477344 0.719336 0.447345
H 3.793551 0.148074 2.969450
H 4.763329 -3.285823 0.817473

H 5.877262 -2.753677 2.067106
H 4.104631 -1.499837 3.553782
Si 1.847185 1.226119 0.260563
O 0.042836 1.547200 0.179565
Cl 1.563901 1.427564 2.412483
Cl 1.633866 0.177742 -1.643622
H 5.456617 -0.436956 3.180590
Cl 2.339069 3.209463 -0.314645
P -1.373153 1.543700 -0.443780
C -2.268826 2.859125 0.420222
C -2.225301 -0.028557 -0.164353
C -1.402938 1.896657 -2.214924
C -1.760560 3.345792 1.631305
C -0.476058 2.799534 -2.754844
C -1.699829 -1.206262 -0.716907
C -2.378329 1.333494 -3.058445
H 0.300033 3.227317 -2.127275
C -0.511744 3.134153 -4.107659
C -3.454081 3.415944 -0.097734
H -0.834386 2.941726 2.028340
C -2.421324 4.362341 2.324609
C -3.390582 -0.107595 0.621168
H -0.785336 -1.170449 -1.301093
C -2.318956 -2.436294 -0.498353
C -3.605199 4.903869 1.805275
H -1.995856 4.722617 3.254308
C -4.118197 4.423816 0.586574
H -3.856051 3.069820 -1.046308
C -2.424972 1.666553 -4.405817
H -3.096849 0.620538 -2.665261
C -3.478170 -2.503473 0.290250
O -4.322773 5.895066 2.397696
H -5.029659 4.863732 0.193488
C -1.489160 2.567813 -4.939639
H 0.232075 3.818817 -4.499013
H -1.885077 -3.329438 -0.932457
O -1.608239 2.822782 -6.270605
H -3.168970 1.231942 -5.066212
C -4.012472 -1.329266 0.846428
H -3.812772 0.788182 1.065752
H -4.909127 -1.398744 1.455718
O -4.150272 -3.651792 0.570822
C -3.859175 6.432112 3.633623
C -0.670662 3.700571 -6.888930
C -3.652365 -4.882972 0.053492
H -0.957048 3.740755 -7.940478

H 0.351372 3.312796 -6.800336
H -0.724363 4.706521 -6.455340
H -4.326645 -5.654760 0.427914
H -2.635267 -5.081667 0.410524
H -3.667238 -4.883552 -1.043303
H -4.581926 7.201314 3.908152
H -2.866276 6.884311 3.521881
H -3.829193 5.660788 4.413114

Table B.87 4-OMe-TPPO aldol TS (2,6-dimethylbenzaldehyde, minor product, 180 degree enolate).



TS Free Energy: -3934.131655

88

C 1.890987 -4.844502 0.079083
C 1.202537 -4.919243 1.291479
C 0.838889 -3.748362 1.949199
C 2.232077 -3.612300 -0.477798
H 0.942605 -5.887576 1.712953

H 2.159277 -5.757408 -0.447356
C 1.883011 -2.408500 0.215861
C 2.935889 -3.605800 -1.821675
C 1.160323 -2.480880 1.439453
H 0.287040 -3.804175 2.885470
C 2.271595 -1.159207 -0.441331
C 0.688815 -1.291546 2.254411
H 2.736697 -1.239483 -1.416889
O 1.786188 -0.016642 -0.125343
C 5.652724 -1.964084 0.451467
C 4.618171 -0.843156 0.467529
C 7.040341 -1.361353 0.197547
C 4.104803 -0.523236 1.854368
O 5.841683 0.128828 -1.376853
H 7.836436 -2.117718 0.208119
H 7.275267 -0.615798 0.967602
C 6.993006 -0.719331 -1.180008
H 6.941944 -1.494189 -1.955430
H 7.858369 -0.082419 -1.386732
C 4.786579 0.136725 -0.522005
O 3.995304 1.103248 -0.864380
H 3.326006 0.234603 1.875159
H 5.450677 -2.694787 -0.344456
H 5.612988 -2.517855 1.395139
H 3.729251 -1.434296 2.336893
Si 2.301553 1.631619 -0.869283
O 0.548553 2.069516 -0.848837
Cl 2.401583 2.415573 1.211412
Cl 2.054329 0.692698 -2.930388
H 4.931883 -0.149444 2.481254
Cl 2.879819 3.556629 -1.714632
P -0.914592 2.092063 -1.342077
C -1.727739 3.374928 -0.359703
C -1.743186 0.508543 -1.054856
C -1.087258 2.497659 -3.092688
C -1.055561 3.930522 0.735600
C -0.158193 3.359995 -3.690868
C -1.405208 -0.599713 -1.846957
C -2.175101 2.030011 -3.854678
H 0.699742 3.714508 -3.128349
C -0.297980 3.743696 -5.024053
C -3.012688 3.846391 -0.690416
H -0.054306 3.589198 0.983867
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C -2.664351 0.336517 -0.005784
H -0.671529 -0.494152 -2.641989

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C -2.936936 5.390299 1.170425
H -1.106323 5.349390 2.339391
C -3.614939 4.838846 0.067633
H -3.542428 3.446449 -1.551388
C -2.323009 2.411053 -5.181946
H -2.903436 1.352641 -3.417880
C -2.904096 -2.004103 -0.570155
O -3.608203 6.363003 1.844871
H -4.603258 5.214632 -0.178879
C -1.381472 3.267826 -5.776449
H 0.449945 4.394206 -5.461901
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O -1.604349 3.571932 -7.083885
H -3.152353 2.048238 -5.781442
C -3.241534 -0.903463 0.233808
H -2.931780 1.175461 0.629430
H -3.955842 -1.044262 1.039405
O -3.522614 -3.174423 -0.259818
C -2.976242 6.984598 2.961084
C -0.669199 4.406199 -7.763796
C -3.209080 -4.341872 -1.015972
H -1.036934 4.484377 -8.787898
H 0.332119 3.958612 -7.765216
H -0.627959 5.404678 -7.311029
H -3.812218 -5.141382 -0.583281
H -2.145496 -4.595043 -0.929081
H -3.476025 -4.212227 -2.072306
H -3.692075 7.719797 3.331584
H -2.050789 7.490933 2.660505
H -2.758309 6.253916 3.749967
H 0.857239 -0.336561 1.766585
H 1.200220 -1.274521 3.225112
H -0.384120 -1.393690 2.461431
H 3.077762 -4.632214 -2.174479
H 3.922584 -3.133157 -1.775014
H 2.362527 -3.069274 -2.587151

## APPENDIX C: X-ray crystallographic data

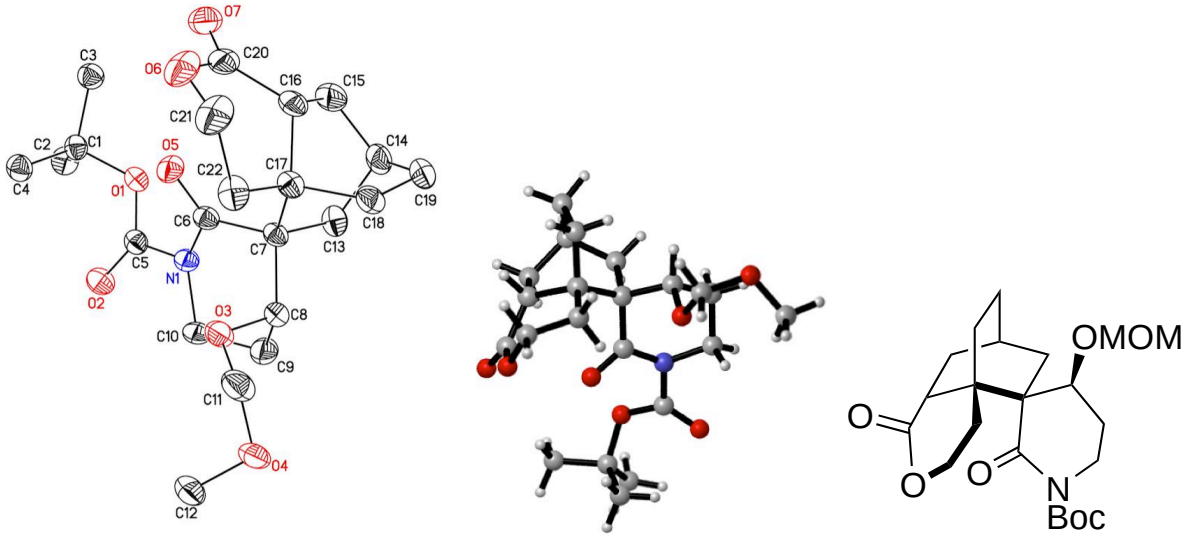



Figure C.1 Structure of bocls.

**Structure Determination.**

Colorless plates of **bocls** were grown from a dichloromethane/hexanes solution of the compound at 22 deg. C. A crystal of dimensions 0.22 x 0.05 x 0.01 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (ë = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ù. The exposure times were 1 sec. for the low angle images, 5 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 30654 reflections to a maximum 2è value of 138.58° of which 3868 were independent and 3749 were greater than 2ó(I). The final cell constants (Table 1) were based on the xyz centroids 15546 reflections above 10ó(I). Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group C2/c with Z = 8 for the formula $C_{22}H_{33}NO_7$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on $F^2$ converged at R1 = 0.0889 and wR2 = 0.2266 [based on I > 2sigma(I)], R1 = 0.0901 and wR2 = 0.2271 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Sheldrick, G.M. SHELXTL, v. 2014/6; Bruker Analytical X-ray, Madison, WI, 2014.
CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku

Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.
CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015).

Table C.1a Crystal data and structure refinement for bocls.

| | |
|---|---|
| Identification code | bocls |
| Empirical formula | C22 H33 N O7 |
| Formula weight | 423.49 |
| Temperature | 85(2) K |
| Wavelength | 1.54184 A |
| Crystal system, space group | Monoclinic, C2/c |
| Unit cell dimensions | a = 18.5695(3) A alpha = 90 deg. |
| | b = 12.26700(10) A beta = 108.953(2) deg. |
| | c = 19.3228(3) A gamma = 90 deg. |
| Volume | 4162.95(11) A^3 |
| Z, Calculated density | 8, 1.351 Mg/m^3 |
| Absorption coefficient | 0.826 mm^-1 |
| F(000) | 1824 |
| Crystal size | 0.220 x 0.050 x 0.010 mm |
| Theta range for data collection | 4.396 to 69.290 deg. |
| Limiting indices | -22<=h<=22, -14<=k<=14, -22<=l<=23 |
| Reflections collected / unique | 30654 / 3868 [R(int) = 0.0625] |
| Completeness to theta = 67.684 | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00000 and 0.48750 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 3868 / 0 / 276 |
| Goodness-of-fit on F^2 | 1.144 |
| Final R indices [I>2sigma(I)] | R1 = 0.0889, wR2 = 0.2266 |
| R indices (all data) | R1 = 0.0901, wR2 = 0.2271 |
| Extinction coefficient | 0.00037(7) |
| Largest diff. peak and hole | 0.419 and -0.415 e.A^-3 |

Table C.2a Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for bocls. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) | |
|---|---|---|---|---|---|
| N(1) | 3501(2) | 6226(3) | 2967(2) | 25(1) | |
| O(1) | 3488(2) | 5876(2) | 4112(2) | 26(1) | |
| O(2) | 4576(2) | 6492(2) | 3946(2) | 32(1) | |
| O(3) | 2875(2) | 7832(2) | 1548(1) | 29(1) | |
| O(4) | 3335(2) | 8222(3) | 579(2) | 45(1) | |
| O(5) | 2417(2) | 6943(2) | 3115(2) | 29(1) | |
| O(6) | 901(2) | 7956(3) | 2741(2) | 43(1) | |
| O(7) | 990(2) | 6456(3) | 3388(2) | 44(1) | |

| | | | | |
|---|---|---|---|---|
| C(1) | 3656(2) | 6266(3) | 4873(2) | 26(1) |
| C(2) | 4315(2) | 5624(4) | 5382(2) | 34(1) |
| C(3) | 2918(2) | 6012(3) | 5032(2) | 31(1) |
| C(4) | 3797(2) | 7484(3) | 4908(2) | 31(1) |
| C(5) | 3908(2) | 6234(3) | 3714(2) | 25(1) |
| C(6) | 2715(2) | 6524(3) | 2707(2) | 24(1) |
| C(7) | 2280(2) | 6262(3) | 1910(2) | 22(1) |
| C(8) | 2767(2) | 6674(3) | 1449(2) | 26(1) |
| C(9) | 3549(2) | 6127(4) | 1705(2) | 33(1) |
| C(10) | 3972(2) | 6419(4) | 2488(2) | 29(1) |
| C(11) | 2770(2) | 8425(4) | 900(2) | 38(1) |
| C(12) | 4065(3) | 8671(5) | 1003(3) | 47(1) |
| C(13) | 2194(2) | 4997(3) | 1785(2) | 29(1) |
| C(14) | 1374(2) | 4626(3) | 1630(2) | 33(1) |
| C(15) | 1104(3) | 5030(4) | 2249(2) | 39(1) |
| C(16) | 972(2) | 6253(4) | 2143(2) | 30(1) |
| C(17) | 1448(2) | 6752(3) | 1685(2) | 24(1) |
| C(18) | 1022(2) | 6362(3) | 903(2) | 28(1) |
| C(19) | 888(2) | 5112(4) | 898(2) | 33(1) |
| C(20) | 979(2) | 6861(4) | 2822(2) | 34(1) |
| C(21) | 784(3) | 8361(4) | 2017(3) | 42(1) |
| C(22) | 1423(2) | 8009(3) | 1740(2) | 32(1) |

Table C.3a Bond lengths [A] and angles [deg] for bocls.

| | |
|---|---|
| N(1)-C(5) | 1.395(5) |
| N(1)-C(6) | 1.428(5) |
| N(1)-C(10) | 1.485(5) |
| O(1)-C(5) | 1.335(5) |
| O(1)-C(1) | 1.480(5) |
| O(2)-C(5) | 1.216(5) |
| O(3)-C(11) | 1.406(5) |
| O(3)-C(8) | 1.439(5) |
| O(4)-C(11) | 1.406(6) |
| O(4)-C(12) | 1.446(5) |
| O(5)-C(6) | 1.213(5) |
| O(6)-C(20) | 1.354(6) |
| O(6)-C(21) | 1.432(6) |
| O(7)-C(20) | 1.196(5) |
| C(1)-C(4) | 1.515(6) |
| C(1)-C(2) | 1.518(5) |
| C(1)-C(3) | 1.530(6) |
| C(2)-H(2A) | 0.9800 |
| C(2)-H(2B) | 0.9800 |

| | |
|---|---|
| C(2)-H(2C) | 0.9800 |
| C(3)-H(3A) | 0.9800 |
| C(3)-H(3B) | 0.9800 |
| C(3)-H(3C) | 0.9800 |
| C(4)-H(4A) | 0.9800 |
| C(4)-H(4B) | 0.9800 |
| C(4)-H(4C) | 0.9800 |
| C(6)-C(7) | 1.522(5) |
| C(7)-C(8) | 1.547(5) |
| C(7)-C(13) | 1.571(5) |
| C(7)-C(17) | 1.581(5) |
| C(8)-C(9) | 1.528(6) |
| C(8)-H(8A) | 1.0000 |
| C(9)-C(10) | 1.503(6) |
| C(9)-H(9A) | 0.9900 |
| C(9)-H(9B) | 0.9900 |
| C(10)-H(10A) | 0.9900 |
| C(10)-H(10B) | 0.9900 |
| C(11)-H(11A) | 0.9900 |
| C(11)-H(11B) | 0.9900 |
| C(12)-H(12A) | 0.9800 |
| C(12)-H(12B) | 0.9800 |
| C(12)-H(12C) | 0.9800 |
| C(13)-C(14) | 1.522(6) |
| C(13)-H(13A) | 0.9900 |
| C(13)-H(13B) | 0.9900 |
| C(14)-C(15) | 1.523(6) |
| C(14)-C(19) | 1.530(6) |
| C(14)-H(14A) | 1.0000 |
| C(15)-C(16) | 1.522(6) |
| C(15)-H(15A) | 0.9900 |
| C(15)-H(15B) | 0.9900 |
| C(16)-C(20) | 1.505(6) |
| C(16)-C(17) | 1.566(5) |
| C(16)-H(16A) | 1.0000 |
| C(17)-C(18) | 1.536(5) |
| C(17)-C(22) | 1.547(5) |
| C(18)-C(19) | 1.552(6) |
| C(18)-H(18A) | 0.9900 |
| C(18)-H(18B) | 0.9900 |
| C(19)-H(19A) | 0.9900 |
| C(19)-H(19B) | 0.9900 |
| C(21)-C(22) | 1.516(6) |
| C(21)-H(21A) | 0.9900 |
| C(21)-H(21B) | 0.9900 |
| C(22)-H(22A) | 0.9900 |

| | |
|---|---|
| C(22)-H(22B) | 0.9900 |
| C(5)-N(1)-C(6) | 120.7(3) |
| C(5)-N(1)-C(10) | 114.4(3) |
| C(6)-N(1)-C(10) | 118.8(3) |
| C(5)-O(1)-C(1) | 119.5(3) |
| C(11)-O(3)-C(8) | 114.8(3) |
| C(11)-O(4)-C(12) | 112.3(3) |
| C(20)-O(6)-C(21) | 115.7(3) |
| O(1)-C(1)-C(4) | 109.9(3) |
| O(1)-C(1)-C(2) | 109.9(3) |
| C(4)-C(1)-C(2) | 113.0(3) |
| O(1)-C(1)-C(3) | 102.7(3) |
| C(4)-C(1)-C(3) | 110.2(3) |
| C(2)-C(1)-C(3) | 110.5(3) |
| C(1)-C(2)-H(2A) | 109.5 |
| C(1)-C(2)-H(2B) | 109.5 |
| H(2A)-C(2)-H(2B) | 109.5 |
| C(1)-C(2)-H(2C) | 109.5 |
| H(2A)-C(2)-H(2C) | 109.5 |
| H(2B)-C(2)-H(2C) | 109.5 |
| C(1)-C(3)-H(3A) | 109.5 |
| C(1)-C(3)-H(3B) | 109.5 |
| H(3A)-C(3)-H(3B) | 109.5 |
| C(1)-C(3)-H(3C) | 109.5 |
| H(3A)-C(3)-H(3C) | 109.5 |
| H(3B)-C(3)-H(3C) | 109.5 |
| C(1)-C(4)-H(4A) | 109.5 |
| C(1)-C(4)-H(4B) | 109.5 |
| H(4A)-C(4)-H(4B) | 109.5 |
| C(1)-C(4)-H(4C) | 109.5 |
| H(4A)-C(4)-H(4C) | 109.5 |
| H(4B)-C(4)-H(4C) | 109.5 |
| O(2)-C(5)-O(1) | 126.1(4) |
| O(2)-C(5)-N(1) | 121.9(4) |
| O(1)-C(5)-N(1) | 111.8(3) |
| O(5)-C(6)-N(1) | 120.6(3) |
| O(5)-C(6)-C(7) | 122.8(3) |
| N(1)-C(6)-C(7) | 116.6(3) |
| C(6)-C(7)-C(8) | 107.3(3) |
| C(6)-C(7)-C(13) | 111.0(3) |
| C(8)-C(7)-C(13) | 106.5(3) |
| C(6)-C(7)-C(17) | 110.4(3) |
| C(8)-C(7)-C(17) | 114.7(3) |
| C(13)-C(7)-C(17) | 106.9(3) |
| O(3)-C(8)-C(9) | 108.2(3) |
| O(3)-C(8)-C(7) | 109.1(3) |

| | |
|---|---|
| C(9)-C(8)-C(7) | 110.0(3) |
| O(3)-C(8)-H(8A) | 109.8 |
| C(9)-C(8)-H(8A) | 109.8 |
| C(7)-C(8)-H(8A) | 109.8 |
| C(10)-C(9)-C(8) | 110.7(3) |
| C(10)-C(9)-H(9A) | 109.5 |
| C(8)-C(9)-H(9A) | 109.5 |
| C(10)-C(9)-H(9B) | 109.5 |
| C(8)-C(9)-H(9B) | 109.5 |
| H(9A)-C(9)-H(9B) | 108.1 |
| N(1)-C(10)-C(9) | 111.6(3 |
| N(1)-C(10)-H(10A) | 109.3 |
| C(9)-C(10)-H(10A) | 109.3 |
| N(1)-C(10)-H(10B) | 109.3 |
| C(9)-C(10)-H(10B) | 109.3 |
| H(10A)-C(10)-H(10B) | 108.0 |
| O(3)-C(11)-O(4) | 113.2(4) |
| O(3)-C(11)-H(11A) | 108.9 |
| O(4)-C(11)-H(11A) | 108.9 |
| O(3)-C(11)-H(11B) | 108.9 |
| O(4)-C(11)-H(11B) | 108.9 |
| H(11A)-C(11)-H(11B) | 107.7 |
| O(4)-C(12)-H(12A) | 109.5 |
| O(4)-C(12)-H(12B) | 109.5 |
| H(12A)-C(12)-H(12B) | 109.5 |
| O(4)-C(12)-H(12C) | 109.5 |
| H(12A)-C(12)-H(12C) | 109.5 |
| H(12B)-C(12)-H(12C) | 109.5 |
| C(14)-C(13)-C(7) | 111.8(3) |
| C(14)-C(13)-H(13A) | 109.3 |
| C(7)-C(13)-H(13A) | 109.3 |
| C(14)-C(13)-H(13B) | 109.3 |
| C(7)-C(13)-H(13B) | 109.3 |
| H(13A)-C(13)-H(13B) | 107.9 |
| C(15)-C(14)-C(13) | 108.2(3) |
| C(15)-C(14)-C(19) | 110.8(4) |
| C(13)-C(14)-C(19) | 108.5(3) |
| C(15)-C(14)-H(14A) | 109.8 |
| C(13)-C(14)-H(14A) | 109.8 |
| C(19)-C(14)-H(14A) | 109.8 |
| C(14)-C(15)-C(16) | 107.1(4) |
| C(14)-C(15)-H(15A) | 110.3 |
| C(16)-C(15)-H(15A) | 110.3 |
| C(14)-C(15)-H(15B) | 110.3 |
| C(16)-C(15)-H(15B) | 110.3 |
| H(15A)-C(15)-H(15B) | 108.5 |

| | |
|---|---|
| C(20)-C(16)-C(15) | 114.6(4) |
| C(20)-C(16)-C(17) | 116.9(4) |
| C(15)-C(16)-C(17) | 111.5(3) |
| C(20)-C(16)-H(16A) | 104.0 |
| C(15)-C(16)-H(16A) | 104.0 |
| C(17)-C(16)-H(16A) | 104.0 |
| C(18)-C(17)-C(22) | 111.2(3) |
| C(18)-C(17)-C(16) | 103.3(3) |
| C(22)-C(17)-C(16) | 108.4(3) |
| C(18)-C(17)-C(7) | 107.3(3) |
| C(22)-C(17)-C(7) | 114.1(3) |
| C(16)-C(17)-C(7) | 112.1(3) |
| C(17)-C(18)-C(19) | 110.2(3) |
| C(17)-C(18)-H(18A) | 109.6 |
| C(19)-C(18)-H(18A) | 109.6 |
| C(17)-C(18)-H(18B) | 109.6 |
| C(19)-C(18)-H(18B) | 109.6 |
| H(18A)-C(18)-H(18B) | 108.1 |
| C(14)-C(19)-C(18) | 109.5(3) |
| C(14)-C(19)-H(19A) | 109.8 |
| C(18)-C(19)-H(19A) | 109.8 |
| C(14)-C(19)-H(19B) | 109.8 |
| C(18)-C(19)-H(19B) | 109.8 |
| H(19A)-C(19)-H(19B) | 108.2 |
| O(7)-C(20)-O(6) | 119.1(4) |
| O(7)-C(20)-C(16) | 125.7(5) |
| O(6)-C(20)-C(16) | 114.9(4) |
| O(6)-C(21)-C(22) | 111.0(3) |
| O(6)-C(21)-H(21A) | 109.4 |
| C(22)-C(21)-H(21A) | 109.4 |
| O(6)-C(21)-H(21B) | 109.4 |
| C(22)-C(21)-H(21B) | 109.4 |
| H(21A)-C(21)-H(21B) | 108.0 |
| C(21)-C(22)-C(17) | 110.7(4) |
| C(21)-C(22)-H(22A) | 109.5 |
| C(17)-C(22)-H(22A) | 109.5 |
| C(21)-C(22)-H(22B) | 109.5 |
| C(17)-C(22)-H(22B) | 109.5 |
| H(22A)-C(22)-H(22B) | 108.1 |

Table C.4a Anisotropic displacement parameters (A^2 x 10^3) for bocls. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|

| | | | | | | |
|---|---|---|---|---|---|---|
| N(1) | 20(2) | 28(2) | 27(2) | -1(1) | 9(1) | 0(1) |
| O(1) | 23(1) | 25(1) | 30(1) | 0(1) | 7(1) | -3(1) |
| O(2) | 20(1) | 37(2) | 36(2) | 2(1) | 5(1) | 2(1) |
| O(3) | 26(1) | 33(2) | 28(1) | 2(1) | 8(1) | -7(1) |
| O(4) | 39(2) | 68(2) | 30(2) | -2(2) | 13(1) | -30(2) |
| O(5) | 21(1) | 35(2) | 31(1) | -6(1) | 8(1) | 7(1) |
| O(6) | 31(2) | 55(2) | 40(2) | -9(2) | 10(1) | 19(2) |
| O(7) | 30(2) | 70(2) | 32(2) | -5(2) | 12(1) | -4(2) |
| C(1) | 25(2) | 27(2) | 26(2) | -1(2) | 5(2) | -1(2) |
| C(2) | 32(2) | 34(2) | 33(2) | 4(2) | 6(2) | 5(2) |
| C(3) | 31(2) | 30(2) | 33(2) | 1(2) | 11(2) | -1(2) |
| C(4) | 32(2) | 24(2) | 37(2) | -1(2) | 12(2) | 0(2) |
| C(5) | 24(2) | 21(2) | 31(2) | -1(2) | 9(2) | 1(2) |
| C(6) | 20(2) | 21(2) | 30(2) | 1(2) | 10(2) | 1(2) |
| C(7) | 17(2) | 19(2) | 29(2) | 0(1) | 8(1) | 1(1) |
| C(8) | 23(2) | 28(2) | 26(2) | -3(2) | 9(2) | -5(2) |
| C(9) | 26(2) | 43(3) | 33(2) | -6(2) | 12(2) | 0(2) |
| C(10) | 18(2) | 37(2) | 35(2) | -1(2) | 12(2) | 1(2) |
| C(11) | 31(2) | 47(3) | 31(2) | 7(2) | 4(2) | -12(2) |
| C(12) | 43(3) | 60(3) | 37(2) | -7(2) | 13(2) | -28(2) |
| C(13) | 30(2) | 20(2) | 33(2) | -1(2) | 5(2) | 3(2) |
| C(14) | 40(2) | 23(2) | 36(2) | -3(2) | 12(2) | -11(2) |
| C(15) | 42(3) | 39(3) | 39(2) | 2(2) | 18(2) | -12(2) |
| C(16) | 16(2) | 40(2) | 33(2) | -1(2) | 6(2) | -2(2) |
| C(17) | 18(2) | 22(2) | 29(2) | 1(2) | 6(2) | 3(1) |
| C(18) | 20(2) | 32(2) | 31(2) | 0(2) | 6(2) | -2(2) |
| C(19) | 31(2) | 33(2) | 33(2) | -5(2) | 8(2) | -10(2) |
| C(20) | 15(2) | 56(3) | 31(2) | -4(2) | 6(2) | 2(2) |
| C(21) | 36(2) | 44(3) | 45(3) | -4(2) | 11(2) | 21(2) |
| C(22) | 29(2) | 26(2) | 36(2) | -1(2) | 6(2) | 8(2) |

Table C.5a Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for bocls.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2A) | 4236 | 4844 | 5271 | 51 |
| H(2B) | 4343 | 5755 | 5890 | 51 |
| H(2C) | 4791 | 5857 | 5312 | 51 |
| H(3A) | 2486 | 6336 | 4651 | 46 |
| H(3B) | 2946 | 6316 | 5509 | 46 |
| H(3C) | 2849 | 5220 | 5038 | 46 |

| | | | | |
|---|---|---|---|---|
| H(4A) | 4267 | 7637 | 4799 | 46 |
| H(4B) | 3847 | 7750 | 5400 | 46 |
| H(4C) | 3369 | 7852 | 4548 | 46 |
| H(8A) | 2504 | 6507 | 920 | 31 |
| H(9A) | 3486 | 5326 | 1660 | 40 |
| H(9B) | 3847 | 6365 | 1391 | 40 |
| H(10A) | 4442 | 5977 | 2665 | 35 |
| H(10B) | 4121 | 7197 | 2517 | 35 |
| H(11A) | 2766 | 9214 | 1009 | 45 |
| H(11B) | 2267 | 8238 | 545 | 45 |
| H(12A) | 4441 | 8510 | 759 | 70 |
| H(12B) | 4019 | 9462 | 1045 | 70 |
| H(12C) | 4230 | 8345 | 1493 | 70 |
| H(13A) | 2365 | 4794 | 1368 | 35 |
| H(13B) | 2524 | 4616 | 2225 | 35 |
| H(14A) | 1347 | 3812 | 1605 | 40 |
| H(15A) | 1493 | 4879 | 2729 | 46 |
| H(15B) | 626 | 4658 | 2234 | 46 |
| H(16A) | 433 | 6313 | 1813 | 36 |
| H(18A) | 1324 | 6539 | 579 | 34 |
| H(18B) | 527 | 6743 | 714 | 34 |
| H(19A) | 343 | 4962 | 817 | 39 |
| H(19B) | 1027 | 4772 | 494 | 39 |
| H(21A) | 757 | 9167 | 2020 | 51 |
| H(21B) | 293 | 8084 | 1684 | 51 |
| H(22A) | 1915 | 8276 | 2078 | 38 |
| H(22B) | 1346 | 8334 | 1253 | 38 |

Table C.6a Torsion angles [deg] for bocls.

| | |
|---|---|
| C(5)-O(1)-C(1)-C(4) | 43.7(4) |
| C(5)-O(1)-C(1)-C(2) | -81.4(4) |
| C(5)-O(1)-C(1)-C(3) | 161.0(3) |
| C(1)-O(1)-C(5)-O(2) | 31.1(6) |
| C(1)-O(1)-C(5)-N(1) | -152.3(3) |
| C(6)-N(1)-C(5)-O(2) | -144.8(4) |
| C(10)-N(1)-C(5)-O(2) | 7.3(5) |
| C(6)-N(1)-C(5)-O(1) | 38.5(5) |
| C(10)-N(1)-C(5)-O(1) | -169.4(3) |
| C(5)-N(1)-C(6)-O(5) | 11.1(6) |
| C(10)-N(1)-C(6)-O(5) | -139.8(4) |
| C(5)-N(1)-C(6)-C(7) | -167.4(3) |
| C(10)-N(1)-C(6)-C(7) | 41.7(5) |
| O(5)-C(6)-C(7)-C(8) | 133.3(4) |

| | |
|---|---|
| N(1)-C(6)-C(7)-C(8) | -48.3(4) |
| O(5)-C(6)-C(7)-C(13) | -110.8(4) |
| N(1)-C(6)-C(7)-C(13) | 67.6(4) |
| O(5)-C(6)-C(7)-C(17) | 7.6(5) |
| N(1)-C(6)-C(7)-C(17) | -174.0(3) |
| C(11)-O(3)-C(8)-C(9) | 105.3(4) |
| C(11)-O(3)-C(8)-C(7) | -135.1(3) |
| C(6)-C(7)-C(8)-O(3) | -60.4(4) |
| C(13)-C(7)-C(8)-O(3) | -179.3(3) |
| C(17)-C(7)-C(8)-O(3) | 62.7(4) |
| C(6)-C(7)-C(8)-C(9) | 58.2(4) |
| C(13)-C(7)-C(8)-C(9) | -60.7(4) |
| C(17)-C(7)-C(8)-C(9) | -178.8(3) |
| O(3)-C(8)-C(9)-C(10) | 57.0(4) |
| C(7)-C(8)-C(9)-C(10) | -62.1(4) |
| C(5)-N(1)-C(10)-C(9) | 165.8(3) |
| C(6)-N(1)-C(10)-C(9) | -41.5(5) |
| C(8)-C(9)-C(10)-N(1) | 51.0(5) |
| C(8)-O(3)-C(11)-O(4) | -68.4(4) |
| C(12)-O(4)-C(11)-O(3) | -70.0(5) |
| C(6)-C(7)-C(13)-C(14) | 110.0(4) |
| C(8)-C(7)-C(13)-C(14) | -133.5(3) |
| C(17)-C(7)-C(13)-C(14) | -10.4(4) |
| C(7)-C(13)-C(14)-C(15) | -54.3(5) |
| C(7)-C(13)-C(14)-C(19) | 65.9(4) |
| C(13)-C(14)-C(15)-C(16) | 73.9(4) |
| C(19)-C(14)-C(15)-C(16) | -44.9(4) |
| C(14)-C(15)-C(16)-C(20) | -159.0(3) |
| C(14)-C(15)-C(16)-C(17) | -23.5(5) |
| C(20)-C(16)-C(17)-C(18) | -151.6(3) |
| C(15)-C(16)-C(17)-C(18) | 74.0(4) |
| C(20)-C(16)-C(17)-C(22) | -33.5(5) |
| C(15)-C(16)-C(17)-C(22) | -168.0(3) |
| C(20)-C(16)-C(17)-C(7) | 93.3(4) |
| C(15)-C(16)-C(17)-C(7) | -41.2(4) |
| C(6)-C(7)-C(17)-C(18) | -174.6(3) |
| C(8)-C(7)-C(17)-C(18) | 64.1(4) |
| C(13)-C(7)-C(17)-C(18) | -53.7(4) |
| C(6)-C(7)-C(17)-C(22) | 61.8(4) |
| C(8)-C(7)-C(17)-C(22) | -59.6(4) |
| C(13)-C(7)-C(17)-C(22) | -177.4(3) |
| C(6)-C(7)-C(17)-C(16) | -61.9(4) |
| C(8)-C(7)-C(17)-C(16) | 176.8(3) |
| C(13)-C(7)-C(17)-C(16) | 59.0(4) |
| C(22)-C(17)-C(18)-C(19) | -166.6(3) |
| C(16)-C(17)-C(18)-C(19) | -50.6(4) |

| | |
|---|---|
| C(7)-C(17)-C(18)-C(19) | 68.0(4) |
| C(15)-C(14)-C(19)-C(18) | 66.5(4) |
| C(13)-C(14)-C(19)-C(18) | -52.1(5) |
| C(17)-C(18)-C(19)-C(14) | -12.8(5) |
| C(21)-O(6)-C(20)-O(7) | -171.4(4) |
| C(21)-O(6)-C(20)-C(16) | 3.2(5) |
| C(15)-C(16)-C(20)-O(7) | -9.1(6) |
| C(17)-C(16)-C(20)-O(7) | -142.1(4) |
| C(15)-C(16)-C(20)-O(6) | 176.8(3) |
| C(17)-C(16)-C(20)-O(6) | 43.7(5) |
| C(20)-O(6)-C(21)-C(22) | -56.6(5) |
| O(6)-C(21)-C(22)-C(17) | 62.5(5) |
| C(18)-C(17)-C(22)-C(21) | 96.4(4) |
| C(16)-C(17)-C(22)-C(21) | -16.5(4) |
| C(7)-C(17)-C(22)-C(21) | -142.1(4) |

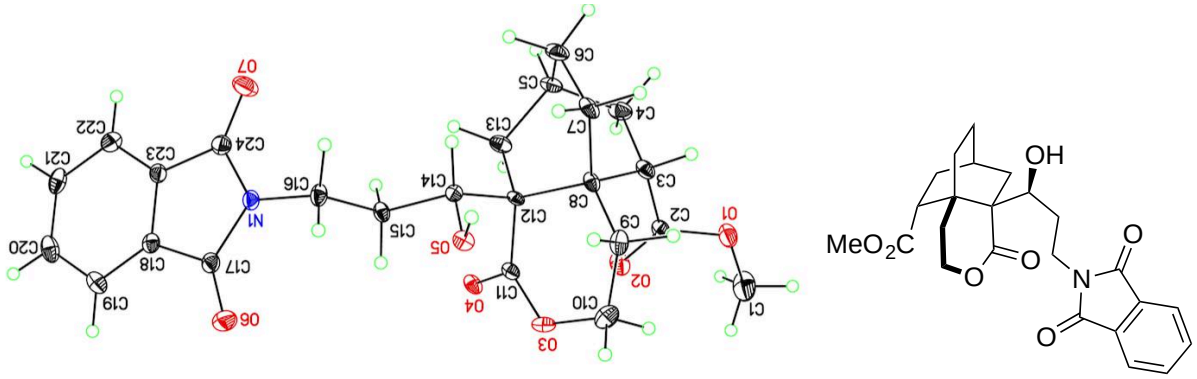



Figure C.2 Structure of ydraph2.

**Structure Determination.**

Colorless blocks of **ydraph2** were grown from a dichloromethane/hexanes solution of the compound at 22 deg. C. A crystal of dimensions 0.26 x 0.15 x 0.15 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (ë = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ù. The exposure times were 1 sec. for the low angle images, 2 sec. for high angle. The integration of the data yielded a total of 36653 reflections to a maximum 2è value of 136.48° of which 4348 were independent and 4304 were greater than 2ó(I). The final cell constants (Table 1) were based on the xyz centroids 18277 reflections above 10ó(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group P2(1)/n with Z = 4 for the formula $C_{25}H_{29}NO_7Cl_2$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in a mix of idealized and refined positions. Full

matrix least-squares refinement based on $F^2$ converged at R1 = 0.0706 and wR2 = 0.1980[based on I > 2sigma(I)], R1 = 0.0709 and wR2 = 0.1982 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.
Sheldrick, G.M. SHELXTL, v. 2014/6; Bruker Analytical X-ray, Madison, WI, 2014.
CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

Table C.1b Crystal data and structure refinement for ydraph2.

| | |
|---|---|
| Identification code | ydraph2 |
| Empirical formula | C25 H29 Cl2 N O7 |
| Formula weight | 526.39 |
| Temperature | 85(2) K |
| Wavelength | 1.54178 A |
| Crystal system, space group | Monoclinic, P2(1)/n |
| Unit cell dimensions | a = 8.4578(2) A alpha = 90 deg. |
| | b = 25.6834(5) A beta = 101.150(7) deg. |
| | c = 11.2552(8) A gamma = 90 deg. |
| Volume | 2398.76(19) A^3 |
| Z, Calculated density | 4, 1.458 Mg/m^3 |
| Absorption coefficient | 2.843 mm^-1 |
| F(000) | 1104 |
| Crystal size | 0.260 x 0.150 x 0.150 mm |
| Theta range for data collection | 6.542 to 68.244 deg. |
| Limiting indices | -10<=h<=10, -30<=k<=30, -13<=l<=12 |
| Reflections collected / unique | 36653 / 4348 [R(int) = 0.0614] |
| Completeness to theta = 67.679 | 99.1 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.861 and 0.693 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 4348 / 1 / 322 |
| Goodness-of-fit on F^2 | 1.061 |
| Final R indices [I>2sigma(I)] | R1 = 0.0706, wR2 = 0.1980 |
| R indices (all data) | R1 = 0.0709, wR2 = 0.1982 |
| Extinction coefficient | 0.0129(9) |
| Largest diff. peak and hole | 0.857 and -1.114 e.A^-3 |

Table C.2b Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for ydraph2. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| N(1) | 7165(3) | 5779(1) | 6956(2) | 13(1) |
| O(1) | 1305(3) | 8942(1) | 6802(2) | 22(1) |

| | | | | |
|---|---|---|---|---|
| O(2) | 1818(3) | 8246(1) | 5750(2) | 18(1) |
| O(3) | 5088(3) | 8000(1) | 5801(2) | 16(1) |
| O(4) | 3674(2) | 7301(1) | 5220(2) | 14(1) |
| O(5) | 7255(2) | 7394(1) | 7825(2) | 12(1) |
| O(6) | 8703(3) | 5981(1) | 5525(2) | 21(1) |
| O(7) | 5585(3) | 5336(1) | 8080(2) | 24(1) |
| C(1) | 592(5) | 9178(2) | 5658(3) | 33(1) |
| C(2) | 1887(3) | 8461(1) | 6710(3) | 13(1) |
| C(3) | 2491(3) | 8227(1) | 7941(2) | 13(1) |
| C(4) | 1172(4) | 7838(1) | 8201(3) | 18(1) |
| C(5) | 1956(4) | 7313(1) | 8533(3) | 15(1) |
| C(6) | 3244(4) | 7366(1) | 9686(3) | 18(1) |
| C(7) | 4466(4) | 7792(1) | 9496(2) | 14(1) |
| C(8) | 4186(3) | 7960(1) | 8151(2) | 11(1) |
| C(9) | 5456(4) | 8351(1) | 7936(3) | 16(1) |
| C(10) | 5488(4) | 8441(1) | 6608(3) | 20(1) |
| C(11) | 4248(3) | 7589(1) | 6054(2) | 11(1) |
| C(12) | 4222(3) | 7459(1) | 7367(2) | 9(1) |
| C(13) | 2724(3) | 7122(1) | 7486(3) | 14(1) |
| C(14) | 5784(3) | 7118(1) | 7801(2) | 10(1) |
| C(15) | 5871(3) | 6639(1) | 7006(2) | 12(1) |
| C(16) | 7256(4) | 6282(1) | 7581(3) | 14(1) |
| C(17) | 7901(3) | 5676(1) | 5964(3) | 14(1) |
| C(18) | 7490(3) | 5126(1) | 5611(3) | 12(1) |
| C(19) | 7919(4) | 4823(1) | 4709(3) | 17(1) |
| C(20) | 7396(4) | 4307(1) | 4628(3) | 19(1) |
| C(21) | 6445(4) | 4109(1) | 5406(3) | 17(1) |
| C(22) | 5993(4) | 4420(1) | 6303(3) | 16(1) |
| C(23) | 6537(3) | 4929(1) | 6390(3) | 13(1) |
| C(24) | 6325(4) | 5350(1) | 7254(3) | 15(1) |
| Cl(1) | 1332(1) | 5913(1) | 8833(1) | 50(1) |
| Cl(2) | 348(1) | 4839(1) | 8310(1) | 44(1) |
| C(25) | 1945(5) | 5258(2) | 8978(4) | 40(1) |

Table C.3b Bond lengths [A] and angles [deg] for ydraph2.

| | |
|---|---|
| N(1)-C(24) | 1.386(4) |
| N(1)-C(17) | 1.404(4) |
| N(1)-C(16) | 1.467(4) |
| O(1)-C(2) | 1.342(4) |
| O(1)-C(1) | 1.445(4) |
| O(2)-C(2) | 1.204(4) |
| O(3)-C(11) | 1.332(4) |
| O(3)-C(10) | 1.451(4) |

| | |
|---|---|
| O(4)-C(11) | 1.220(4) |
| O(5)-C(14) | 1.428(3) |
| O(5)-H(5) | 0.83(2) |
| O(6)-C(17) | 1.203(4) |
| O(7)-C(24) | 1.217(4) |
| C(1)-H(1A) | 0.9800 |
| C(1)-H(1B) | 0.9800 |
| C(1)-H(1C) | 0.9800 |
| C(2)-C(3) | 1.505(4) |
| C(3)-C(8) | 1.565(4) |
| C(3)-C(4) | 1.566(4) |
| C(3)-H(3) | 1.0000 |
| C(4)-C(5) | 1.519(4) |
| C(4)-H(4A) | 0.9900 |
| C(4)-H(4B) | 0.9900 |
| C(5)-C(6) | 1.531(4) |
| C(5)-C(13) | 1.532(4) |
| C(5)-H(5A) | 1.0000 |
| C(6)-C(7) | 1.549(4) |
| C(6)-H(6A) | 0.9900 |
| C(6)-H(6B) | 0.9900 |
| C(7)-C(8) | 1.548(4) |
| C(7)-H(7A) | 0.9900 |
| C(7)-H(7B) | 0.9900 |
| C(8)-C(9) | 1.524(4) |
| C(8)-C(12) | 1.564(4) |
| C(9)-C(10) | 1.518(4) |
| C(9)-H(9A) | 0.9900 |
| C(9)-H(9B) | 0.9900 |
| C(10)-H(10A) | 0.9900 |
| C(10)-H(10B) | 0.9900 |
| C(11)-C(12) | 1.520(4) |
| C(12)-C(13) | 1.562(4) |
| C(12)-C(14) | 1.582(4) |
| C(13)-H(13A) | 0.9900 |
| C(13)-H(13B) | 0.9900 |
| C(14)-C(15) | 1.532(4) |
| C(14)-H(14) | 1.0000 |
| C(15)-C(16) | 1.529(4) |
| C(15)-H(15A) | 0.9900 |
| C(15)-H(15B) | 0.9900 |
| C(16)-H(16A) | 0.9900 |
| C(16)-H(16B) | 0.9900 |
| C(17)-C(18) | 1.491(4) |
| C(18)-C(19) | 1.382(4) |
| C(18)-C(23) | 1.395(4) |

| | |
|---|---|
| C(19)-C(20) | 1.396(5) |
| C(19)-H(19) | 0.9500 |
| C(20)-C(21) | 1.394(5) |
| C(20)-H(20) | 0.9500 |
| C(21)-C(22) | 1.399(4) |
| C(21)-H(21) | 0.9500 |
| C(22)-C(23) | 1.383(4) |
| C(22)-H(22) | 0.9500 |
| C(23)-C(24) | 1.488(4) |
| Cl(1)-C(25) | 1.757(4) |
| Cl(2)-C(25) | 1.777(4) |
| C(25)-H(25A) | 0.9900 |
| C(25)-H(25B) | 0.9900 |
| C(24)-N(1)-C(17) | 111.8(2) |
| C(24)-N(1)-C(16) | 124.4(2) |
| C(17)-N(1)-C(16) | 123.8(2) |
| C(2)-O(1)-C(1) | 114.4(2) |
| C(11)-O(3)-C(10) | 123.6(2) |
| C(14)-O(5)-H(5) | 112(4) |
| O(1)-C(1)-H(1A) | 109.5 |
| O(1)-C(1)-H(1B) | 109.5 |
| H(1A)-C(1)-H(1B) | 109.5 |
| O(1)-C(1)-H(1C) | 109.5 |
| H(1A)-C(1)-H(1C) | 109.5 |
| H(1B)-C(1)-H(1C) | 109.5 |
| O(2)-C(2)-O(1) | 122.5(3) |
| O(2)-C(2)-C(3) | 126.3(3) |
| O(1)-C(2)-C(3) | 111.1(2) |
| C(2)-C(3)-C(8) | 116.8(2) |
| C(2)-C(3)-C(4) | 107.4(2) |
| C(8)-C(3)-C(4) | 110.9(2) |
| C(2)-C(3)-H(3) | 107.1 |
| C(8)-C(3)-H(3) | 107.1 |
| C(4)-C(3)-H(3) | 107.1 |
| C(5)-C(4)-C(3) | 108.6(2) |
| C(5)-C(4)-H(4A) | 110.0 |
| C(3)-C(4)-H(4A) | 110.0 |
| C(5)-C(4)-H(4B) | 110.0 |
| C(3)-C(4)-H(4B) | 110.0 |
| H(4A)-C(4)-H(4B) | 108.3 |
| C(4)-C(5)-C(6) | 109.5(3) |
| C(4)-C(5)-C(13) | 109.0(2) |
| C(6)-C(5)-C(13) | 110.1(2) |
| C(4)-C(5)-H(5A) | 109.4 |
| C(6)-C(5)-H(5A) | 109.4 |
| C(13)-C(5)-H(5A) | 109.4 |

| | |
|---|---|
| C(5)-C(6)-C(7) | 109.3(2) |
| C(5)-C(6)-H(6A) | 109.8 |
| C(7)-C(6)-H(6A) | 109.8 |
| C(5)-C(6)-H(6B) | 109.8 |
| C(7)-C(6)-H(6B) | 109.8 |
| H(6A)-C(6)-H(6B) | 108.3 |
| C(8)-C(7)-C(6) | 110.6(2) |
| C(8)-C(7)-H(7A) | 109.5 |
| C(6)-C(7)-H(7A) | 109.5 |
| C(8)-C(7)-H(7B) | 109.5 |
| C(6)-C(7)-H(7B) | 109.5 |
| H(7A)-C(7)-H(7B) | 108.1 |
| C(9)-C(8)-C(7) | 111.0(2) |
| C(9)-C(8)-C(12) | 111.2(2) |
| C(7)-C(8)-C(12) | 107.8(2) |
| C(9)-C(8)-C(3) | 109.9(2) |
| C(7)-C(8)-C(3) | 103.4(2) |
| C(12)-C(8)-C(3) | 113.1(2) |
| C(10)-C(9)-C(8) | 113.8(2) |
| C(10)-C(9)-H(9A) | 108.8 |
| C(8)-C(9)-H(9A) | 108.8 |
| C(10)-C(9)-H(9B) | 108.8 |
| C(8)-C(9)-H(9B) | 108.8 |
| H(9A)-C(9)-H(9B) | 107.7 |
| O(3)-C(10)-C(9) | 116.9(2) |
| O(3)-C(10)-H(10A) | 108.1 |
| C(9)-C(10)-H(10A) | 108.1 |
| O(3)-C(10)-H(10B) | 108.1 |
| C(9)-C(10)-H(10B) | 108.1 |
| H(10A)-C(10)-H(10B) | 107.3 |
| O(4)-C(11)-O(3) | 117.7(2) |
| O(4)-C(11)-C(12) | 122.5(3) |
| O(3)-C(11)-C(12) | 119.4(2) |
| C(11)-C(12)-C(13) | 111.7(2) |
| C(11)-C(12)-C(8) | 111.9(2) |
| C(13)-C(12)-C(8) | 107.6(2) |
| C(11)-C(12)-C(14) | 104.7(2) |
| C(13)-C(12)-C(14) | 108.0(2) |
| C(8)-C(12)-C(14) | 112.8(2) |
| C(5)-C(13)-C(12) | 111.1(2) |
| C(5)-C(13)-H(13A) | 109.4 |
| C(12)-C(13)-H(13A) | 109.4 |
| C(5)-C(13)-H(13B) | 109.4 |
| C(12)-C(13)-H(13B) | 109.4 |
| H(13A)-C(13)-H(13B) | 108.0 |
| O(5)-C(14)-C(15) | 105.7(2) |

| | |
|---|---|
| O(5)-C(14)-C(12) | 113.8(2) |
| C(15)-C(14)-C(12) | 113.3(2) |
| O(5)-C(14)-H(14) | 107.9 |
| C(15)-C(14)-H(14) | 107.9 |
| C(12)-C(14)-H(14) | 107.9 |
| C(16)-C(15)-C(14) | 110.7(2) |
| C(16)-C(15)-H(15A) | 109.5 |
| C(14)-C(15)-H(15A) | 109.5 |
| C(16)-C(15)-H(15B) | 109.5 |
| C(14)-C(15)-H(15B) | 109.5 |
| H(15A)-C(15)-H(15B) | 108.1 |
| N(1)-C(16)-C(15) | 111.1(2) |
| N(1)-C(16)-H(16A) | 109.4 |
| C(15)-C(16)-H(16A) | 109.4 |
| N(1)-C(16)-H(16B) | 109.4 |
| C(15)-C(16)-H(16B) | 109.4 |
| H(16A)-C(16)-H(16B) | 108.0 |
| O(6)-C(17)-N(1) | 125.3(3) |
| O(6)-C(17)-C(18) | 128.9(3) |
| N(1)-C(17)-C(18) | 105.8(2) |
| C(19)-C(18)-C(23) | 121.6(3) |
| C(19)-C(18)-C(17) | 130.4(3) |
| C(23)-C(18)-C(17) | 108.0(2) |
| C(18)-C(19)-C(20) | 117.3(3) |
| C(18)-C(19)-H(19) | 121.4 |
| C(20)-C(19)-H(19) | 121.4 |
| C(21)-C(20)-C(19) | 121.3(3) |
| C(21)-C(20)-H(20) | 119.4 |
| C(19)-C(20)-H(20) | 119.4 |
| C(20)-C(21)-C(22) | 121.1(3) |
| C(20)-C(21)-H(21) | 119.5 |
| C(22)-C(21)-H(21) | 119.5 |
| C(23)-C(22)-C(21) | 117.3(3) |
| C(23)-C(22)-H(22) | 121.3 |
| C(21)-C(22)-H(22) | 121.3 |
| C(22)-C(23)-C(18) | 121.5(3) |
| C(22)-C(23)-C(24) | 130.8(3) |
| C(18)-C(23)-C(24) | 107.8(3) |
| O(7)-C(24)-N(1) | 124.9(3) |
| O(7)-C(24)-C(23) | 128.5(3) |
| N(1)-C(24)-C(23) | 106.6(2) |
| Cl(1)-C(25)-Cl(2) | 110.7(2) |
| Cl(1)-C(25)-H(25A) | 109.5 |
| Cl(2)-C(25)-H(25A) | 109.5 |
| Cl(1)-C(25)-H(25B) | 109.5 |
| Cl(2)-C(25)-H(25B) | 109.5 |

| | |
|---|---|
| H(25A)-C(25)-H(25B) | 108.1 |

Table C.4b Anisotropic displacement parameters (A^2 x 10^3) for ydraph2. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| N(1) | 16(1) | 10(1) | 12(1) | -2(1) | 2(1) | 1(1) |
| O(1) | 34(1) | 19(1) | 12(1) | 1(1) | 3(1) | 12(1) |
| O(2) | 22(1) | 21(1) | 9(1) | -3(1) | -2(1) | 4(1) |
| O(3) | 18(1) | 20(1) | 12(1) | 4(1) | 7(1) | -2(1) |
| O(4) | 16(1) | 19(1) | 7(1) | -2(1) | 1(1) | 5(1) |
| O(5) | 10(1) | 15(1) | 11(1) | -2(1) | 1(1) | -2(1) |
| O(6) | 25(1) | 17(1) | 22(1) | 2(1) | 9(1) | -4(1) |
| O(7) | 34(1) | 21(1) | 21(1) | -6(1) | 16(1) | -7(1) |
| C(1) | 54(2) | 26(2) | 16(2) | 4(1) | -2(2) | 19(2) |
| C(2) | 9(1) | 15(1) | 13(1) | -1(1) | 2(1) | 3(1) |
| C(3) | 14(1) | 18(1) | 9(1) | -1(1) | 1(1) | 5(1) |
| C(4) | 14(1) | 26(2) | 17(2) | 4(1) | 6(1) | 4(1) |
| C(5) | 14(1) | 22(2) | 11(1) | 2(1) | 6(1) | 2(1) |
| C(6) | 20(2) | 25(2) | 8(1) | 3(1) | 4(1) | 5(1) |
| C(7) | 16(1) | 20(2) | 5(1) | -3(1) | -1(1) | 5(1) |
| C(8) | 12(1) | 13(1) | 7(1) | -3(1) | -1(1) | 3(1) |
| C(9) | 15(1) | 12(1) | 19(2) | -3(1) | 0(1) | 1(1) |
| C(10) | 21(2) | 16(2) | 24(2) | 2(1) | 4(1) | -5(1) |
| C(11) | 9(1) | 16(1) | 9(1) | 1(1) | 2(1) | 5(1) |
| C(12) | 10(1) | 13(1) | 5(1) | -1(1) | 2(1) | 1(1) |
| C(13) | 12(1) | 20(2) | 11(1) | -2(1) | 2(1) | -3(1) |
| C(14) | 10(1) | 10(1) | 7(1) | -1(1) | 0(1) | 0(1) |
| C(15) | 12(1) | 12(1) | 10(1) | -3(1) | 1(1) | 2(1) |
| C(16) | 18(1) | 10(1) | 12(1) | -2(1) | 0(1) | 2(1) |
| C(17) | 14(1) | 14(1) | 13(1) | 1(1) | 1(1) | 3(1) |
| C(18) | 11(1) | 13(1) | 12(1) | 1(1) | -1(1) | 2(1) |
| C(19) | 16(1) | 21(2) | 16(2) | -4(1) | 4(1) | 2(1) |
| C(20) | 17(2) | 20(2) | 17(2) | -8(1) | -2(1) | 4(1) |
| C(21) | 19(2) | 11(1) | 19(2) | -3(1) | -4(1) | 1(1) |
| C(22) | 19(2) | 15(2) | 15(1) | 1(1) | 1(1) | -1(1) |
| C(23) | 14(1) | 12(1) | 11(1) | 0(1) | 2(1) | 2(1) |
| C(24) | 18(1) | 15(1) | 13(1) | 0(1) | 3(1) | 1(1) |
| Cl(1) | 43(1) | 35(1) | 68(1) | 6(1) | 1(1) | 0(1) |
| Cl(2) | 40(1) | 38(1) | 50(1) | 1(1) | 2(1) | -6(1) |
| C(25) | 35(2) | 36(2) | 46(2) | 4(2) | 4(2) | -1(2) |

Table C.5b Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for ydraph2.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(5) | 7770(50) | 7440(20) | 8530(20) | 43(13) |
| H(1A) | 1416 | 9219 | 5161 | 50 |
| H(1B) | 153 | 9520 | 5804 | 50 |
| H(1C) | -277 | 8955 | 5234 | 50 |
| H(3) | 2556 | 8516 | 8544 | 16 |
| H(4A) | 686 | 7970 | 8876 | 22 |
| H(4B) | 308 | 7804 | 7474 | 22 |
| H(5A) | 1119 | 7058 | 8676 | 18 |
| H(6A) | 3809 | 7030 | 9876 | 21 |
| H(6B) | 2731 | 7461 | 10376 | 21 |
| H(7A) | 4347 | 8098 | 10007 | 17 |
| H(7B) | 5577 | 7657 | 9747 | 17 |
| H(9A) | 5252 | 8688 | 8309 | 19 |
| H(9B) | 6529 | 8226 | 8350 | 19 |
| H(10A) | 4728 | 8726 | 6311 | 24 |
| H(10B) | 6580 | 8562 | 6547 | 24 |
| H(13A) | 1919 | 7140 | 6721 | 17 |
| H(13B) | 3057 | 6754 | 7626 | 17 |
| H(14) | 5773 | 6994 | 8642 | 12 |
| H(15A) | 4841 | 6445 | 6900 | 14 |
| H(15B) | 6032 | 6751 | 6196 | 14 |
| H(16A) | 8296 | 6452 | 7544 | 17 |
| H(16B) | 7211 | 6225 | 8444 | 17 |
| H(19) | 8545 | 4961 | 4167 | 20 |
| H(20) | 7693 | 4086 | 4030 | 23 |
| H(21) | 6099 | 3756 | 5325 | 21 |
| H(22) | 5340 | 4288 | 6831 | 20 |
| H(25A) | 2287 | 5171 | 9846 | 47 |
| H(25B) | 2878 | 5206 | 8579 | 47 |

Table C.6b Torsion angles [deg] for ydraph2.

| | |
|---|---|
| C(1)-O(1)-C(2)-O(2) | 0.1(4) |
| C(1)-O(1)-C(2)-C(3) | -175.6(3) |
| O(2)-C(2)-C(3)-C(8) | 51.4(4) |
| O(1)-C(2)-C(3)-C(8) | -133.0(3) |

| | |
|---|---|
| O(2)-C(2)-C(3)-C(4) | -73.9(4) |
| O(1)-C(2)-C(3)-C(4) | 101.7(3) |
| C(2)-C(3)-C(4)-C(5) | 126.6(3) |
| C(8)-C(3)-C(4)-C(5) | -2.1(3) |
| C(3)-C(4)-C(5)-C(6) | 61.9(3) |
| C(3)-C(4)-C(5)-C(13) | -58.6(3) |
| C(4)-C(5)-C(6)-C(7) | -55.7(3) |
| C(13)-C(5)-C(6)-C(7) | 64.1(3) |
| C(5)-C(6)-C(7)-C(8) | -9.9(3) |
| C(6)-C(7)-C(8)-C(9) | -176.0(2) |
| C(6)-C(7)-C(8)-C(12) | -53.9(3) |
| C(6)-C(7)-C(8)-C(3) | 66.2(3) |
| C(2)-C(3)-C(8)-C(9) | 58.6(3) |
| C(4)-C(3)-C(8)-C(9) | -178.0(2) |
| C(2)-C(3)-C(8)-C(7) | 177.2(2) |
| C(4)-C(3)-C(8)-C(7) | -59.3(3) |
| C(2)-C(3)-C(8)-C(12) | -66.4(3) |
| C(4)-C(3)-C(8)-C(12) | 57.1(3) |
| C(7)-C(8)-C(9)-C(10) | 167.0(2) |
| C(12)-C(8)-C(9)-C(10) | 46.9(3) |
| C(3)-C(8)-C(9)-C(10) | -79.2(3) |
| C(11)-O(3)-C(10)-C(9) | 21.3(4) |
| C(8)-C(9)-C(10)-O(3) | -33.1(4) |
| C(10)-O(3)-C(11)-O(4) | 163.8(3) |
| C(10)-O(3)-C(11)-C(12) | -24.0(4) |
| O(4)-C(11)-C(12)-C(13) | -30.2(4) |
| O(3)-C(11)-C(12)-C(13) | 158.0(2) |
| O(4)-C(11)-C(12)-C(8) | -151.0(3) |
| O(3)-C(11)-C(12)-C(8) | 37.2(3) |
| O(4)-C(11)-C(12)-C(14) | 86.5(3) |
| O(3)-C(11)-C(12)-C(14) | -85.4(3) |
| C(9)-C(8)-C(12)-C(11) | -48.2(3) |
| C(7)-C(8)-C(12)-C(11) | -170.1(2) |
| C(3)-C(8)-C(12)-C(11) | 76.1(3) |
| C(9)-C(8)-C(12)-C(13) | -171.2(2) |
| C(7)-C(8)-C(12)-C(13) | 66.8(3) |
| C(3)-C(8)-C(12)-C(13) | -47.0(3) |
| C(9)-C(8)-C(12)-C(14) | 69.6(3) |
| C(7)-C(8)-C(12)-C(14) | -52.3(3) |
| C(3)-C(8)-C(12)-C(14) | -166.1(2) |
| C(4)-C(5)-C(13)-C(12) | 69.6(3) |
| C(6)-C(5)-C(13)-C(12) | -50.5(3) |
| C(11)-C(12)-C(13)-C(5) | -136.9(2) |
| C(8)-C(12)-C(13)-C(5) | -13.7(3) |
| C(14)-C(12)-C(13)-C(5) | 108.5(3) |
| C(11)-C(12)-C(14)-O(5) | 65.3(3) |

| | |
|---|---|
| C(13)-C(12)-C(14)-O(5) | -175.5(2) |
| C(8)-C(12)-C(14)-O(5) | -56.6(3) |
| C(11)-C(12)-C(14)-C(15) | -55.5(3) |
| C(13)-C(12)-C(14)-C(15) | 63.7(3) |
| C(8)-C(12)-C(14)-C(15) | -177.4(2) |
| O(5)-C(14)-C(15)-C(16) | 63.7(3) |
| C(12)-C(14)-C(15)-C(16) | -171.1(2) |
| C(24)-N(1)-C(16)-C(15) | -89.1(3) |
| C(17)-N(1)-C(16)-C(15) | 89.7(3) |
| C(14)-C(15)-C(16)-N(1) | 169.2(2) |
| C(24)-N(1)-C(17)-O(6) | -179.9(3) |
| C(16)-N(1)-C(17)-O(6) | 1.2(4) |
| C(24)-N(1)-C(17)-C(18) | -0.4(3) |
| C(16)-N(1)-C(17)-C(18) | -179.4(2) |
| O(6)-C(17)-C(18)-C(19) | 0.5(5) |
| N(1)-C(17)-C(18)-C(19) | -178.9(3) |
| O(6)-C(17)-C(18)-C(23) | 179.7(3) |
| N(1)-C(17)-C(18)-C(23) | 0.3(3) |
| C(23)-C(18)-C(19)-C(20) | -1.7(4) |
| C(17)-C(18)-C(19)-C(20) | 177.4(3) |
| C(18)-C(19)-C(20)-C(21) | 1.5(4) |
| C(19)-C(20)-C(21)-C(22) | -0.5(5) |
| C(20)-C(21)-C(22)-C(23) | -0.5(4) |
| C(21)-C(22)-C(23)-C(18) | 0.3(4) |
| C(21)-C(22)-C(23)-C(24) | -177.7(3) |
| C(19)-C(18)-C(23)-C(22) | 0.8(4) |
| C(17)-C(18)-C(23)-C(22) | -178.5(3) |
| C(19)-C(18)-C(23)-C(24) | 179.2(3) |
| C(17)-C(18)-C(23)-C(24) | -0.1(3) |
| C(17)-N(1)-C(24)-O(7) | 179.8(3) |
| C(16)-N(1)-C(24)-O(7) | -1.3(5) |
| C(17)-N(1)-C(24)-C(23) | 0.4(3) |
| C(16)-N(1)-C(24)-C(23) | 179.4(2) |
| C(22)-C(23)-C(24)-O(7) | -1.3(5) |
| C(18)-C(23)-C(24)-O(7) | -179.5(3) |
| C(22)-C(23)-C(24)-N(1) | 178.0(3) |
| C(18)-C(23)-C(24)-N(1) | -0.2(3) |

Table C.7b Hydrogen bonds for ydraph2 [A and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(5)-H(5)...O(4)#1 | 0.83(2) | 2.03(2) | 2.840(3) | 166(5) |

Symmetry transformations used to generate equivalent atoms:
#1 x+1/2,-y+3/2,z+1/2

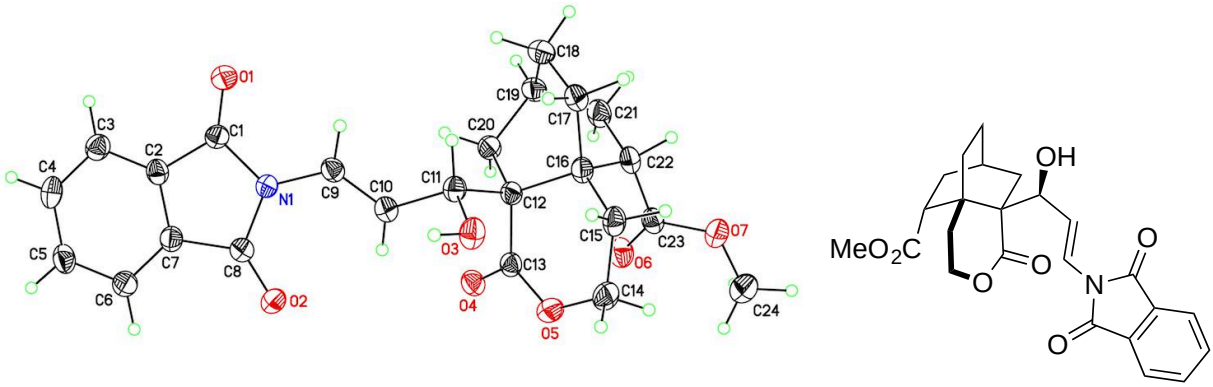



Figure C.3 Structure of ydrap.

**Structure Determination.**

Colorless needles of **ydrap** were grown from a dichloromethane/acetone/hexanes solution of the compound at 25 deg. C. A crystal of dimensions 0.10 x 0.10 x 0.09 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (ë = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 3655 images were collected with an oscillation width of 1.0° in ù. The exposure times were 2 sec. for the low angle images, 12 sec. for high angle. The integration of the data yielded a total of 51157 reflections to a maximum 2è value of 136.48° of which 3752 were independent and 3655 were greater than 2ó(I). The final cell constants (Table 1) were based on the xyz centroids 39417 reflections above 10ó(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package, using the space group Pna2(1) with Z = 4 for the formula $C_{24}H_{25}NO_7$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in a combination of idealized and refined positions. Full matrix least-squares refinement based on $F^2$ converged at R1 = 0.0366 and wR2 = 0.0963 [based on I > 2sigma(I)], R1 = 0.0371 and wR2 = 0.0967 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Sheldrick, G.M. SHELXTL, v. 2008/4; Bruker Analytical X-ray, Madison, WI, 2008.

CrystalClear Expert 2.0 r12, Rigaku Americas and Rigaku Corporation (2011), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

Table C.1c Crystal data and structure refinement for ydrap.

| | |
|---|---|
| Identification code | ydrap |

| | |
|---|---|
| Empirical formula | C24 H25 N O7 |
| Formula weight | 439.45 |
| Temperature | 85(2) K |
| Wavelength | 1.54178 A |
| Crystal system, space group | Orthorhombic, Pna2(1) |
| Unit cell dimensions | a = 15.9063(11) A alpha = 90 deg. |
| | b = 12.5570(2) A beta = 90 deg. |
| | c = 10.2614(2) A gamma = 90 deg. |
| Volume | 2049.56(15) A^3 |
| Z, Calculated density | 4, 1.424 Mg/m^3 |
| Absorption coefficient | 0.873 mm^-1 |
| F(000) | 928 |
| Crystal size | 0.10 x 0.10 x 0.09 mm |
| Theta range for data collection | 4.49 to 68.24 deg. |
| Limiting indices | -19<=h<=19, -15<=k<=14, -12<=l<=12 |
| Reflections collected / unique | 51157 / 3752 [R(int) = 0.0976] |
| Completeness to theta = 68.24 | 100.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9255 and 0.9177 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 3752 / 1 / 295 |
| Goodness-of-fit on F^2 | 1.078 |
| Final R indices [I>2sigma(I)] | R1 = 0.0366, wR2 = 0.0963 |
| R indices (all data) | R1 = 0.0371, wR2 = 0.0967 |
| Absolute structure parameter | 0.33(17) |
| Largest diff. peak and hole | 0.183 and -0.217 e.A^-3 |

Table C.2c Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for ydrap. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| N(1) | 2922(1) | 4269(1) | 5909(2) | 22(1) |
| O(1) | 1894(1) | 4770(1) | 7387(2) | 29(1) |
| O(2) | 3664(1) | 3312(1) | 4341(2) | 34(1) |
| O(3) | 5536(1) | 5574(1) | 6492(2) | 30(1) |
| O(4) | 4958(1) | 6134(1) | 3122(2) | 29(1) |
| O(5) | 6221(1) | 6297(1) | 3934(2) | 30(1) |
| O(6) | 5945(1) | 8406(1) | 2687(2) | 36(1) |
| O(7) | 6964(1) | 9278(1) | 3764(2) | 35(1) |

| | | | | |
|---|---|---|---|---|
| C(1) | 2133(1) | 4195(2) | 6521(2) | 23(1) |
| C(2) | 1696(1) | 3280(2) | 5893(2) | 24(1) |
| C(3) | 893(1) | 2895(2) | 6070(2) | 28(1) |
| C(4) | 671(1) | 1983(2) | 5380(2) | 32(1) |
| C(5) | 1243(1) | 1477(2) | 4563(2) | 31(1) |
| C(6) | 2046(1) | 1892(2) | 4354(2) | 30(1) |
| C(7) | 2251(1) | 2806(2) | 5027(2) | 26(1) |
| C(8) | 3044(1) | 3441(2) | 5000(2) | 25(1) |
| C(9) | 3497(1) | 5075(2) | 6243(2) | 24(1) |
| C(10) | 4176(1) | 5344(2) | 5578(2) | 24(1) |
| C(11) | 4793(1) | 6132(2) | 6132(2) | 24(1) |
| C(12) | 5029(1) | 7057(2) | 5166(2) | 22(1) |
| C(13) | 5399(1) | 6495(2) | 3989(2) | 23(1) |
| C(14) | 6839(1) | 6734(2) | 4829(2) | 31(1) |
| C(15) | 6518(1) | 7379(2) | 5983(2) | 27(1) |
| C(16) | 5647(1) | 7878(2) | 5773(2) | 24(1) |
| C(17) | 5280(1) | 8269(2) | 7082(2) | 28(1) |
| C(18) | 4378(1) | 8709(2) | 6863(2) | 32(1) |
| C(19) | 4182(1) | 8758(2) | 5405(2) | 30(1) |
| C(20) | 4192(1) | 7638(2) | 4822(2) | 26(1) |
| C(21) | 4841(1) | 9428(2) | 4705(2) | 32(1) |
| C(22) | 5723(1) | 8923(2) | 4935(2) | 26(1) |
| C(23) | 6200(1) | 8820(2) | 3670(2) | 26(1) |
| C(24) | 7482(2) | 9249(2) | 2609(3) | 41(1) |

Table C.3c Bond lengths [A] and angles [deg] for ydrap.

| | |
|---|---|
| N(1)-C(9) | 1.406(2) |
| N(1)-C(1) | 1.407(2) |
| N(1)-C(8) | 1.410(3) |
| O(1)-C(1) | 1.206(2) |
| O(2)-C(8) | 1.207(2) |
| O(3)-C(11) | 1.423(2) |
| O(3)-H(3) | 0.84(4) |
| O(4)-C(13) | 1.219(3) |
| O(5)-C(13) | 1.333(2) |
| O(5)-C(14) | 1.453(3) |
| O(6)-C(23) | 1.205(3) |
| O(7)-C(23) | 1.348(2) |
| O(7)-C(24) | 1.444(3) |
| C(1)-C(2) | 1.489(3) |
| C(2)-C(3) | 1.378(3) |
| C(2)-C(7) | 1.388(3) |
| C(3)-C(4) | 1.392(3) |
| C(3)-H(3A) | 0.9500 |

| | |
|---|---|
| C(4)-C(5) | 1.391(3) |
| C(4)-H(4) | 0.9500 |
| C(5)-C(6) | 1.397(3) |
| C(5)-H(5) | 0.9500 |
| C(6)-C(7) | 1.379(3) |
| C(6)-H(6) | 0.9500 |
| C(7)-C(8) | 1.493(3) |
| C(9)-C(10) | 1.322(3) |
| C(9)-H(9) | 0.9500 |
| C(10)-C(11) | 1.505(3) |
| C(10)-H(10) | 0.9500 |
| C(11)-C(12) | 1.572(3) |
| C(11)-H(11) | 1.0000 |
| C(12)-C(13) | 1.518(3) |
| C(12)-C(16) | 1.556(3) |
| C(12)-C(20) | 1.558(2) |
| C(14)-C(15) | 1.523(3) |
| C(14)-H(14A) | 0.9900 |
| C(14)-H(14B) | 0.9900 |
| C(15)-C(16) | 1.535(3) |
| C(15)-H(15A) | 0.9900 |
| C(15)-H(15B) | 0.9900 |
| C(16)-C(17) | 1.544(3) |
| C(16)-C(22) | 1.573(3) |
| C(17)-C(18) | 1.554(3) |
| C(17)-H(17A) | 0.9900 |
| C(17)-H(17B) | 0.9900 |
| C(18)-C(19) | 1.530(3) |
| C(18)-H(18A) | 0.9900 |
| C(18)-H(18B) | 0.9900 |
| C(19)-C(21) | 1.525(3) |
| C(19)-C(20) | 1.527(3) |
| C(19)-H(19) | 1.0000 |
| C(20)-H(20A) | 0.9900 |
| C(20)-H(20B) | 0.9900 |
| C(21)-C(22) | 1.557(3) |
| C(21)-H(21A) | 0.9900 |
| C(21)-H(21B) | 0.9900 |
| C(22)-C(23) | 1.509(3) |
| C(22)-H(22) | 1.0000 |
| C(24)-H(24A) | 0.9800 |
| C(24)-H(24B) | 0.9800 |
| C(24)-H(24C) | 0.9800 |
| C(9)-N(1)-C(1) | 121.26(16) |
| C(9)-N(1)-C(8) | 127.06(16) |
| C(1)-N(1)-C(8) | 111.66(15) |

| | |
|---|---|
| C(11)-O(3)-H(3) | 104(2) |
| C(13)-O(5)-C(14) | 124.52(16) |
| C(23)-O(7)-C(24) | 116.46(18) |
| O(1)-C(1)-N(1) | 124.73(18) |
| O(1)-C(1)-C(2) | 129.33(18) |
| N(1)-C(1)-C(2) | 105.93(16) |
| C(3)-C(2)-C(7) | 121.59(19) |
| C(3)-C(2)-C(1) | 130.27(18) |
| C(7)-C(2)-C(1) | 108.13(16) |
| C(2)-C(3)-C(4) | 117.20(19) |
| C(2)-C(3)-H(3A) | 121.4 |
| C(4)-C(3)-H(3A) | 121.4 |
| C(5)-C(4)-C(3) | 121.12(18) |
| C(5)-C(4)-H(4) | 119.4 |
| C(3)-C(4)-H(4) | 119.4 |
| C(4)-C(5)-C(6) | 121.4(2) |
| C(4)-C(5)-H(5) | 119.3 |
| C(6)-C(5)-H(5) | 119.3 |
| C(7)-C(6)-C(5) | 116.74(19) |
| C(7)-C(6)-H(6) | 121.6 |
| C(5)-C(6)-H(6) | 121.6 |
| C(6)-C(7)-C(2) | 121.85(19) |
| C(6)-C(7)-C(8) | 129.47(18) |
| C(2)-C(7)-C(8) | 108.67(17) |
| O(2)-C(8)-N(1) | 125.62(18) |
| O(2)-C(8)-C(7) | 128.96(18) |
| N(1)-C(8)-C(7) | 105.41(15) |
| C(10)-C(9)-N(1) | 126.08(18) |
| C(10)-C(9)-H(9) | 117.0 |
| N(1)-C(9)-H(9) | 117.0 |
| C(9)-C(10)-C(11) | 120.36(18) |
| C(9)-C(10)-H(10) | 119.8 |
| C(11)-C(10)-H(10) | 119.8 |
| O(3)-C(11)-C(10) | 108.42(16) |
| O(3)-C(11)-C(12) | 109.27(15) |
| C(10)-C(11)-C(12) | 113.78(16) |
| O(3)-C(11)-H(11) | 108.4 |
| C(10)-C(11)-H(11) | 108.4 |
| C(12)-C(11)-H(11) | 108.4 |
| C(13)-C(12)-C(16) | 112.47(15) |
| C(13)-C(12)-C(20) | 111.63(16) |
| C(16)-C(12)-C(20) | 108.68(16) |
| C(13)-C(12)-C(11) | 104.48(15) |
| C(16)-C(12)-C(11) | 112.84(15) |
| C(20)-C(12)-C(11) | 106.59(15) |
| O(4)-C(13)-O(5) | 117.64(18) |

| | |
|---|---|
| O(4)-C(13)-C(12) | 122.03(17) |
| O(5)-C(13)-C(12) | 120.06(17) |
| O(5)-C(14)-C(15) | 117.78(16) |
| O(5)-C(14)-H(14A) | 107.9 |
| C(15)-C(14)-H(14A) | 107.9 |
| O(5)-C(14)-H(14B) | 107.9 |
| C(15)-C(14)-H(14B) | 107.9 |
| H(14A)-C(14)-H(14B) | 107.2 |
| C(14)-C(15)-C(16) | 114.22(17) |
| C(14)-C(15)-H(15A) | 108.7 |
| C(16)-C(15)-H(15A) | 108.7 |
| C(14)-C(15)-H(15B) | 108.7 |
| C(16)-C(15)-H(15B) | 108.7 |
| H(15A)-C(15)-H(15B) | 107.6 |
| C(15)-C(16)-C(17) | 110.39(16) |
| C(15)-C(16)-C(12) | 110.85(16) |
| C(17)-C(16)-C(12) | 108.64(15) |
| C(15)-C(16)-C(22) | 110.39(15) |
| C(17)-C(16)-C(22) | 103.86(16) |
| C(12)-C(16)-C(22) | 112.46(16) |
| C(16)-C(17)-C(18) | 109.67(17) |
| C(16)-C(17)-H(17A) | 109.7 |
| C(18)-C(17)-H(17A) | 109.7 |
| C(16)-C(17)-H(17B) | 109.7 |
| C(18)-C(17)-H(17B) | 109.7 |
| H(17A)-C(17)-H(17B) | 108.2 |
| C(19)-C(18)-C(17) | 110.11(17) |
| C(19)-C(18)-H(18A) | 109.6 |
| C(17)-C(18)-H(18A) | 109.6 |
| C(19)-C(18)-H(18B) | 109.6 |
| C(17)-C(18)-H(18B) | 109.6 |
| H(18A)-C(18)-H(18B) | 108.2 |
| C(21)-C(19)-C(20) | 108.44(18) |
| C(21)-C(19)-C(18) | 110.00(18) |
| C(20)-C(19)-C(18) | 110.14(18) |
| C(21)-C(19)-H(19) | 109.4 |
| C(20)-C(19)-H(19) | 109.4 |
| C(18)-C(19)-H(19) | 109.4 |
| C(19)-C(20)-C(12) | 110.59(16) |
| C(19)-C(20)-H(20A) | 109.5 |
| C(12)-C(20)-H(20A) | 109.5 |
| C(19)-C(20)-H(20B) | 109.5 |
| C(12)-C(20)-H(20B) | 109.5 |
| H(20A)-C(20)-H(20B) | 108.1 |
| C(19)-C(21)-C(22) | 108.86(17) |
| C(19)-C(21)-H(21A) | 109.9 |

| | |
|---|---|
| C(22)-C(21)-H(21A) | 109.9 |
| C(19)-C(21)-H(21B) | 109.9 |
| C(22)-C(21)-H(21B) | 109.9 |
| H(21A)-C(21)-H(21B) | 108.3 |
| C(23)-C(22)-C(21) | 110.96(17) |
| C(23)-C(22)-C(16) | 115.91(16) |
| C(21)-C(22)-C(16) | 110.71(16) |
| C(23)-C(22)-H(22) | 106.2 |
| C(21)-C(22)-H(22) | 106.2 |
| C(16)-C(22)-H(22) | 106.2 |
| O(6)-C(23)-O(7) | 123.13(19) |
| O(6)-C(23)-C(22) | 126.03(17) |
| O(7)-C(23)-C(22) | 110.83(17) |
| O(7)-C(24)-H(24A) | 109.5 |
| O(7)-C(24)-H(24B) | 109.5 |
| H(24A)-C(24)-H(24B) | 109.5 |
| O(7)-C(24)-H(24C) | 109.5 |
| H(24A)-C(24)-H(24C) | 109.5 |
| H(24B)-C(24)-H(24C) | 109.5 |

Table C.4c Anisotropic displacement parameters (A^2 x 10^3) for ydrap. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| N(1) | 19(1) | 22(1) | 26(1) | -1(1) | 1(1) | -1(1) |
| O(1) | 25(1) | 28(1) | 35(1) | -4(1) | 3(1) | 1(1) |
| O(2) | 27(1) | 36(1) | 39(1) | -10(1) | 10(1) | -6(1) |
| O(3) | 23(1) | 28(1) | 39(1) | 8(1) | -4(1) | -1(1) |
| O(4) | 32(1) | 28(1) | 28(1) | -4(1) | -1(1) | -5(1) |
| O(5) | 24(1) | 32(1) | 33(1) | -3(1) | 2(1) | 3(1) |
| O(6) | 36(1) | 37(1) | 34(1) | 0(1) | -4(1) | -7(1) |
| O(7) | 25(1) | 40(1) | 40(1) | -4(1) | 2(1) | -7(1) |
| C(1) | 20(1) | 22(1) | 27(1) | 3(1) | 0(1) | 4(1) |
| C(2) | 24(1) | 20(1) | 28(1) | 3(1) | -2(1) | -1(1) |
| C(3) | 24(1) | 29(1) | 31(1) | 3(1) | 1(1) | 0(1) |
| C(4) | 25(1) | 34(1) | 36(1) | 6(1) | -3(1) | -10(1) |
| C(5) | 37(1) | 28(1) | 29(1) | -2(1) | -1(1) | -11(1) |
| C(6) | 31(1) | 30(1) | 28(1) | -4(1) | 2(1) | -4(1) |
| C(7) | 24(1) | 24(1) | 29(1) | 1(1) | 0(1) | -2(1) |
| C(8) | 25(1) | 24(1) | 25(1) | -1(1) | 1(1) | 0(1) |
| C(9) | 22(1) | 21(1) | 27(1) | -2(1) | -3(1) | 0(1) |
| C(10) | 25(1) | 22(1) | 26(1) | 0(1) | -2(1) | -2(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(11) | 22(1) | 24(1) | 25(1) | 1(1) | -2(1) | -2(1) |
| C(12) | 19(1) | 22(1) | 26(1) | -2(1) | -2(1) | -1(1) |
| C(13) | 22(1) | 20(1) | 28(1) | 3(1) | 0(1) | -1(1) |
| C(14) | 19(1) | 32(1) | 41(1) | 0(1) | -3(1) | 2(1) |
| C(15) | 21(1) | 27(1) | 33(1) | 2(1) | -6(1) | -3(1) |
| C(16) | 22(1) | 23(1) | 28(1) | 0(1) | -2(1) | -3(1) |
| C(17) | 28(1) | 26(1) | 29(1) | -4(1) | -1(1) | -5(1) |
| C(18) | 30(1) | 30(1) | 37(1) | -10(1) | 2(1) | 1(1) |
| C(19) | 25(1) | 23(1) | 41(1) | -4(1) | 0(1) | 4(1) |
| C(20) | 20(1) | 25(1) | 32(1) | -2(1) | -3(1) | 1(1) |
| C(21) | 29(1) | 22(1) | 45(1) | 3(1) | -3(1) | 1(1) |
| C(22) | 25(1) | 21(1) | 32(1) | 1(1) | -4(1) | -5(1) |
| C(23) | 25(1) | 21(1) | 32(1) | 1(1) | -4(1) | -1(1) |
| C(24) | 34(1) | 47(1) | 43(1) | -3(1) | 7(1) | -4(1) |

Table C.5c Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for ydrap.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(3) | 5350(20) | 5030(30) | 6880(40) | 66(11) |
| H(3A) | 507 | 3237 | 6639 | 34 |
| H(4) | 120 | 1702 | 5470 | 38 |
| H(5) | 1083 | 836 | 4137 | 38 |
| H(6) | 2433 | 1560 | 3776 | 36 |
| H(9) | 3387 | 5462 | 7020 | 28 |
| H(10) | 4275 | 5038 | 4745 | 29 |
| H(11) | 4542 | 6453 | 6934 | 28 |
| H(14A) | 7225 | 7193 | 4322 | 37 |
| H(14B) | 7176 | 6134 | 5175 | 37 |
| H(15A) | 6926 | 7955 | 6172 | 32 |
| H(15B) | 6494 | 6910 | 6758 | 32 |
| H(17A) | 5643 | 8835 | 7448 | 33 |
| H(17B) | 5263 | 7672 | 7711 | 33 |
| H(18A) | 3965 | 8243 | 7305 | 39 |
| H(18B) | 4333 | 9431 | 7245 | 39 |
| H(19) | 3614 | 9082 | 5273 | 36 |
| H(20A) | 4133 | 7684 | 3863 | 31 |
| H(20B) | 3711 | 7225 | 5166 | 31 |
| H(21A) | 4832 | 10166 | 5045 | 38 |
| H(21B) | 4717 | 9452 | 3760 | 38 |
| H(22) | 6044 | 9444 | 5479 | 31 |
| H(24A) | 7637 | 8511 | 2416 | 62 |
| H(24B) | 7992 | 9671 | 2755 | 62 |

| | | | | |
|---|---|---|---|---|
| H(24C) | 7169 | 9547 | 1872 | 62 |

Table C.6c Torsion angles [deg] for ydrap.

| | |
|---|---|
| C(9)-N(1)-C(1)-O(1) | -2.5(3) |
| C(8)-N(1)-C(1)-O(1) | 175.75(18) |
| C(9)-N(1)-C(1)-C(2) | 178.23(16) |
| C(8)-N(1)-C(1)-C(2) | -3.5(2) |
| O(1)-C(1)-C(2)-C(3) | 4.7(4) |
| N(1)-C(1)-C(2)-C(3) | -176.1(2) |
| O(1)-C(1)-C(2)-C(7) | -174.7(2) |
| N(1)-C(1)-C(2)-C(7) | 4.5(2) |
| C(7)-C(2)-C(3)-C(4) | 2.4(3) |
| C(1)-C(2)-C(3)-C(4) | -176.9(2) |
| C(2)-C(3)-C(4)-C(5) | 0.9(3) |
| C(3)-C(4)-C(5)-C(6) | -3.1(3) |
| C(4)-C(5)-C(6)-C(7) | 1.9(3) |
| C(5)-C(6)-C(7)-C(2) | 1.4(3) |
| C(5)-C(6)-C(7)-C(8) | -179.1(2) |
| C(3)-C(2)-C(7)-C(6) | -3.7(3) |
| C(1)-C(2)-C(7)-C(6) | 175.78(19) |
| C(3)-C(2)-C(7)-C(8) | 176.72(18) |
| C(1)-C(2)-C(7)-C(8) | -3.8(2) |
| C(9)-N(1)-C(8)-O(2) | -1.7(3) |
| C(1)-N(1)-C(8)-O(2) | -179.8(2) |
| C(9)-N(1)-C(8)-C(7) | 179.39(18) |
| C(1)-N(1)-C(8)-C(7) | 1.3(2) |
| C(6)-C(7)-C(8)-O(2) | 3.3(4) |
| C(2)-C(7)-C(8)-O(2) | -177.2(2) |
| C(6)-C(7)-C(8)-N(1) | -177.9(2) |
| C(2)-C(7)-C(8)-N(1) | 1.7(2) |
| C(1)-N(1)-C(9)-C(10) | -166.32(19) |
| C(8)-N(1)-C(9)-C(10) | 15.7(3) |
| N(1)-C(9)-C(10)-C(11) | -172.54(18) |
| C(9)-C(10)-C(11)-O(3) | 108.4(2) |
| C(9)-C(10)-C(11)-C(12) | -129.8(2) |
| O(3)-C(11)-C(12)-C(13) | 62.18(18) |
| C(10)-C(11)-C(12)-C(13) | -59.13(19) |
| O(3)-C(11)-C(12)-C(16) | -60.3(2) |
| C(10)-C(11)-C(12)-C(16) | 178.38(15) |
| O(3)-C(11)-C(12)-C(20) | -179.51(15) |
| C(10)-C(11)-C(12)-C(20) | 59.2(2) |
| C(14)-O(5)-C(13)-O(4) | 175.09(18) |
| C(14)-O(5)-C(13)-C(12) | -10.7(3) |

| | |
|---|---|
| C(16)-C(12)-C(13)-O(4) | -153.16(18) |
| C(20)-C(12)-C(13)-O(4) | -30.7(3) |
| C(11)-C(12)-C(13)-O(4) | 84.1(2) |
| C(16)-C(12)-C(13)-O(5) | 32.9(2) |
| C(20)-C(12)-C(13)-O(5) | 155.35(17) |
| C(11)-C(12)-C(13)-O(5) | -89.84(19) |
| C(13)-O(5)-C(14)-C(15) | 5.9(3) |
| O(5)-C(14)-C(15)-C(16) | -24.2(3) |
| C(14)-C(15)-C(16)-C(17) | 165.83(17) |
| C(14)-C(15)-C(16)-C(12) | 45.4(2) |
| C(14)-C(15)-C(16)-C(22) | -79.9(2) |
| C(13)-C(12)-C(16)-C(15) | -49.2(2) |
| C(20)-C(12)-C(16)-C(15) | -173.36(16) |
| C(11)-C(12)-C(16)-C(15) | 68.7(2) |
| C(13)-C(12)-C(16)-C(17) | -170.72(16) |
| C(20)-C(12)-C(16)-C(17) | 65.2(2) |
| C(11)-C(12)-C(16)-C(17) | -52.8(2) |
| C(13)-C(12)-C(16)-C(22) | 74.9(2) |
| C(20)-C(12)-C(16)-C(22) | -49.2(2) |
| C(11)-C(12)-C(16)-C(22) | -167.22(15) |
| C(15)-C(16)-C(17)-C(18) | -176.63(16) |
| C(12)-C(16)-C(17)-C(18) | -54.9(2) |
| C(22)-C(16)-C(17)-C(18) | 65.04(19) |
| C(16)-C(17)-C(18)-C(19) | -7.6(2) |
| C(17)-C(18)-C(19)-C(21) | -56.4(2) |
| C(17)-C(18)-C(19)-C(20) | 63.1(2) |
| C(21)-C(19)-C(20)-C(12) | 68.0(2) |
| C(18)-C(19)-C(20)-C(12) | -52.5(2) |
| C(13)-C(12)-C(20)-C(19) | -134.90(18) |
| C(16)-C(12)-C(20)-C(19) | -10.3(2) |
| C(11)-C(12)-C(20)-C(19) | 111.59(19) |
| C(20)-C(19)-C(21)-C(22) | -61.6(2) |
| C(18)-C(19)-C(21)-C(22) | 58.9(2) |
| C(19)-C(21)-C(22)-C(23) | 131.70(19) |
| C(19)-C(21)-C(22)-C(16) | 1.5(2) |
| C(15)-C(16)-C(22)-C(23) | 51.9(2) |
| C(17)-C(16)-C(22)-C(23) | 170.24(16) |
| C(12)-C(16)-C(22)-C(23) | -72.5(2) |
| C(15)-C(16)-C(22)-C(21) | 179.41(17) |
| C(17)-C(16)-C(22)-C(21) | -62.3(2) |
| C(12)-C(16)-C(22)-C(21) | 55.0(2) |
| C(24)-O(7)-C(23)-O(6) | -0.2(3) |
| C(24)-O(7)-C(23)-C(22) | -179.06(18) |
| C(21)-C(22)-C(23)-O(6) | -52.1(3) |
| C(16)-C(22)-C(23)-O(6) | 75.3(3) |
| C(21)-C(22)-C(23)-O(7) | 126.75(18) |

| | |
|---|---|
| C(16)-C(22)-C(23)-O(7) | -105.87(19) |

Table C.7c. Hydrogen bonds for ydrap [A and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(3)-H(3)...O(4)#1 | 0.84(4) | 2.00(4) | 2.831(2) | 168(4) |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,z+1/2

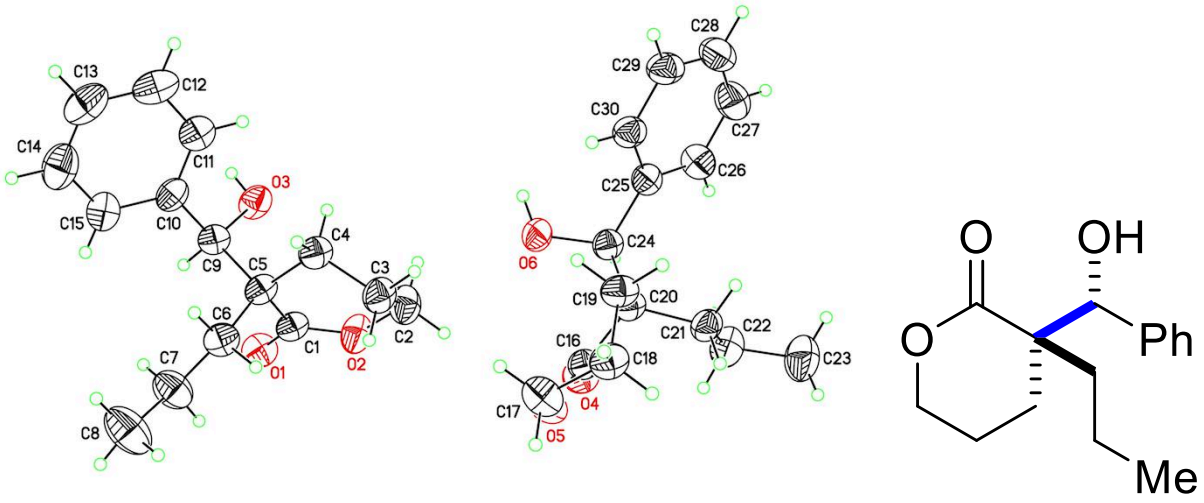



Figure C.4 Structure of ydp3945.

**Structure Determination.**

Colorless needles of **ydp3945** were grown from a dichloromethane/hexanes solution of the compound at 22 deg. C. A crystal of dimensions 0.27 x 0.07 x 0.01 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 225(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ω. The exposure times were 5 sec. for the low angle images, 30 sec. for high angle. The integration of the data yielded a total of 19550 reflections to a maximum 2θ value of 136.48° of which 4550 were independent and 3840 were greater than 2σ(I). The final cell constants (Table 1) were based on the xyz centroids 753 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package, using the space group Pc with Z = 4 for the formula $C_{15}H_{20}O_3$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in a combination of idealized and refined positions. A destructive phase change upon flash cooling of the crystal precluded examination at lower

temperature. Full matrix least-squares refinement based on $F^2$ converged at R1 = 0.0657 and wR2 = 0.1768 [based on I > 2sigma(I)], R1 = 0.0743 and wR2 = 0.1881 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Table C.1d Crystal data and structure refinement for ydp3945.

| | |
|---|---|
| Identification code | ydp3945 |
| Empirical formula | C15 H20 O3 |
| Formula weight | 248.31 |
| Temperature | 225(2) K |
| Wavelength | 1.54178 A |
| Crystal system, space group | Monoclinic, Pc |
| Unit cell dimensions | a = 15.688(2) A alpha = 90 deg. |
| | b = 9.1771(7) A beta = 101.742(7) deg. |
| | c = 9.4276(9) A gamma = 90 deg. |
| Volume | 1328.9(2) A^3 |
| Z, Calculated density | 4, 1.241 Mg/m^3 |
| Absorption coefficient | 0.684 mm^-1 |
| F(000) | 536 |
| Crystal size | 0.25 x 0.07 x 0.01 mm |
| Theta range for data collection | 2.88 to 68.24 deg. |
| Limiting indices | -18<=h<=18, -10<=k<=10, -11<=l<=10 |
| Reflections collected / unique | 19550 / 4550 [R(int) = 0.0902] |
| Completeness to theta = 68.24 | 99.3 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9932 and 0.8475 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 4550 / 2 / 336 |
| Goodness-of-fit on F^2 | 1.067 |
| Final R indices [I>2sigma(I)] | R1 = 0.0657, wR2 = 0.1768 |
| R indices (all data) | R1 = 0.0743, wR2 = 0.1881 |
| Absolute structure parameter | 0.1(3) |
| Largest diff. peak and hole | 0.284 and -0.231 e.A^-3 |

Table C.2d Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for ydp3945. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 3364(2) | 1640(3) | 7934(3) | 50(1) |
| O(2) | 4426(2) | 3089(3) | 7738(3) | 54(1) |
| O(3) | 3680(2) | 777(3) | 4868(3) | 48(1) |

| | | | | |
|---|---|---|---|---|
| O(4) | 6661(2) | 6599(3) | 9019(3) | 50(1) |
| O(5) | 5593(2) | 8057(3) | 8153(3) | 53(1) |
| O(6) | 6311(2) | 5760(3) | 5730(3) | 46(1) |
| C(1) | 3647(2) | 2512(3) | 7181(4) | 39(1) |
| C(2) | 4868(3) | 4100(4) | 6942(5) | 54(1) |
| C(3) | 4237(3) | 4975(4) | 5855(4) | 47(1) |
| C(4) | 3668(2) | 3925(4) | 4858(4) | 43(1) |
| C(5) | 3124(2) | 2957(4) | 5685(4) | 38(1) |
| C(6) | 2316(2) | 3825(4) | 5861(4) | 44(1) |
| C(7) | 1727(3) | 3239(5) | 6828(6) | 58(1) |
| C(8) | 900(3) | 4134(6) | 6673(8) | 81(2) |
| C(9) | 2872(2) | 1499(3) | 4890(4) | 38(1) |
| C(10) | 2318(2) | 1636(3) | 3380(4) | 40(1) |
| C(11) | 2682(3) | 1857(4) | 2174(4) | 46(1) |
| C(12) | 2171(3) | 1924(4) | 783(4) | 55(1) |
| C(13) | 1287(3) | 1758(5) | 595(5) | 62(1) |
| C(14) | 907(3) | 1532(5) | 1763(6) | 64(1) |
| C(15) | 1409(3) | 1473(4) | 3157(5) | 53(1) |
| C(16) | 6361(2) | 7488(3) | 8085(4) | 39(1) |
| C(17) | 5143(3) | 9082(4) | 7083(5) | 53(1) |
| C(18) | 5752(2) | 9956(4) | 6398(4) | 47(1) |
| C(19) | 6313(2) | 8918(4) | 5750(4) | 42(1) |
| C(20) | 6869(2) | 7951(3) | 6920(3) | 36(1) |
| C(21) | 7689(2) | 8812(4) | 7655(4) | 42(1) |
| C(22) | 8317(3) | 8187(5) | 8944(5) | 58(1) |
| C(23) | 9102(3) | 9146(6) | 9427(6) | 72(1) |
| C(24) | 7115(2) | 6497(3) | 6277(4) | 38(1) |
| C(25) | 7643(2) | 6648(3) | 5113(4) | 38(1) |
| C(26) | 8543(2) | 6435(4) | 5431(4) | 49(1) |
| C(27) | 9025(3) | 6525(5) | 4342(5) | 58(1) |
| C(28) | 8618(3) | 6832(4) | 2947(5) | 53(1) |
| C(29) | 7730(3) | 7032(4) | 2599(4) | 48(1) |
| C(30) | 7247(2) | 6929(4) | 3678(4) | 42(1) |

Table C.3d Bond lengths [A] and angles [deg] for ydp3945.

| | |
|---|---|
| O(1)-C(1) | 1.213(4) |
| O(2)-C(1) | 1.337(4) |
| O(2)-C(2) | 1.454(5) |
| O(3)-C(9) | 1.434(4) |
| O(3)-H(3) | 0.87(7) |
| O(4)-C(16) | 1.222(4) |
| O(5)-C(16) | 1.327(4) |
| O(5)-C(17) | 1.453(5) |

| | |
|---|---|
| O(6)-C(24) | 1.431(4) |
| O(6)-H(6) | 0.93(8) |
| C(1)-C(5) | 1.536(5) |
| C(2)-C(3) | 1.504(6) |
| C(2)-H(2A) | 0.9800 |
| C(2)-H(2B) | 0.9800 |
| C(3)-C(4) | 1.505(5) |
| C(3)-H(3A) | 0.9800 |
| C(3)-H(3B) | 0.9800 |
| C(4)-C(5) | 1.548(4) |
| C(4)-H(4A) | 0.9800 |
| C(4)-H(4B) | 0.9800 |
| C(5)-C(6) | 1.535(5) |
| C(5)-C(9) | 1.546(5) |
| C(6)-C(7) | 1.521(6) |
| C(6)-H(6A) | 0.9800 |
| C(6)-H(6B) | 0.9800 |
| C(7)-C(8) | 1.517(6) |
| C(7)-H(7A) | 0.9800 |
| C(7)-H(7B) | 0.9800 |
| C(8)-H(8A) | 0.9700 |
| C(8)-H(8B) | 0.9700 |
| C(8)-H(8C) | 0.9700 |
| C(9)-C(10) | 1.514(5) |
| C(9)-H(9) | 0.9900 |
| C(10)-C(11) | 1.387(5) |
| C(10)-C(15) | 1.406(5) |
| C(11)-C(12) | 1.392(6) |
| C(11)-H(11) | 0.9400 |
| C(12)-C(13) | 1.371(7) |
| C(12)-H(12) | 0.9400 |
| C(13)-C(14) | 1.370(8) |
| C(13)-H(13) | 0.9400 |
| C(14)-C(15) | 1.389(6) |
| C(14)-H(14) | 0.9400 |
| C(15)-H(15) | 0.9400 |
| C(16)-C(20) | 1.542(4) |
| C(17)-C(18) | 1.492(5) |
| C(17)-H(17A) | 0.9800 |
| C(17)-H(17B) | 0.9800 |
| C(18)-C(19) | 1.509(5) |
| C(18)-H(18A) | 0.9800 |
| C(18)-H(18B) | 0.9800 |
| C(19)-C(20) | 1.540(5) |
| C(19)-H(19A) | 0.9800 |
| C(19)-H(19B) | 0.9800 |

| | |
|---|---|
| C(20)-C(24) | 1.546(4) |
| C(20)-C(21) | 1.549(5) |
| C(21)-C(22) | 1.513(6) |
| C(21)-H(21A) | 0.9800 |
| C(21)-H(21B) | 0.9800 |
| C(22)-C(23) | 1.507(6) |
| C(22)-H(22A) | 0.9800 |
| C(22)-H(22B) | 0.9800 |
| C(23)-H(23A) | 0.9700 |
| C(23)-H(23B) | 0.9700 |
| C(23)-H(23C) | 0.9700 |
| C(24)-C(25) | 1.511(5) |
| C(24)-H(24) | 0.9900 |
| C(25)-C(30) | 1.393(5) |
| C(25)-C(26) | 1.397(5) |
| C(26)-C(27) | 1.395(6) |
| C(26)-H(26) | 0.9400 |
| C(27)-C(28) | 1.369(7) |
| C(27)-H(27) | 0.9400 |
| C(28)-C(29) | 1.377(6) |
| C(28)-H(28) | 0.9400 |
| C(29)-C(30) | 1.390(5) |
| C(29)-H(29) | 0.9400 |
| C(30)-H(30) | 0.9400 |
| C(1)-O(2)-C(2) | 122.9(3) |
| C(9)-O(3)-H(3) | 107(4) |
| C(16)-O(5)-C(17) | 122.7(3) |
| C(24)-O(6)-H(6) | 111(4) |
| O(1)-C(1)-O(2) | 116.5(3) |
| O(1)-C(1)-C(5) | 121.5(3) |
| O(2)-C(1)-C(5) | 122.0(3) |
| O(2)-C(2)-C(3) | 112.1(3) |
| O(2)-C(2)-H(2A) | 109.2 |
| C(3)-C(2)-H(2A) | 109.2 |
| O(2)-C(2)-H(2B) | 109.2 |
| C(3)-C(2)-H(2B) | 109.2 |
| H(2A)-C(2)-H(2B) | 107.9 |
| C(2)-C(3)-C(4) | 107.9(3) |
| C(2)-C(3)-H(3A) | 110.1 |
| C(4)-C(3)-H(3A) | 110.1 |
| C(2)-C(3)-H(3B) | 110.1 |
| C(4)-C(3)-H(3B) | 110.1 |
| H(3A)-C(3)-H(3B) | 108.4 |
| C(3)-C(4)-C(5) | 111.7(3) |
| C(3)-C(4)-H(4A) | 109.3 |
| C(5)-C(4)-H(4A) | 109.3 |

| | |
|---|---|
| C(3)-C(4)-H(4B) | 109.3 |
| C(5)-C(4)-H(4B) | 109.3 |
| H(4A)-C(4)-H(4B) | 107.9 |
| C(6)-C(5)-C(1) | 109.7(3) |
| C(6)-C(5)-C(9) | 111.4(3) |
| C(1)-C(5)-C(9) | 104.6(3) |
| C(6)-C(5)-C(4) | 108.0(3) |
| C(1)-C(5)-C(4) | 111.6(3) |
| C(9)-C(5)-C(4) | 111.5(3) |
| C(7)-C(6)-C(5) | 119.8(3) |
| C(7)-C(6)-H(6A) | 107.4 |
| C(5)-C(6)-H(6A) | 107.4 |
| C(7)-C(6)-H(6B) | 107.4 |
| C(5)-C(6)-H(6B) | 107.4 |
| H(6A)-C(6)-H(6B) | 106.9 |
| C(8)-C(7)-C(6) | 111.3(4) |
| C(8)-C(7)-H(7A) | 109.4 |
| C(6)-C(7)-H(7A) | 109.4 |
| C(8)-C(7)-H(7B) | 109.4 |
| C(6)-C(7)-H(7B) | 109.4 |
| H(7A)-C(7)-H(7B) | 108.0 |
| C(7)-C(8)-H(8A) | 109.5 |
| C(7)-C(8)-H(8B) | 109.5 |
| H(8A)-C(8)-H(8B) | 109.5 |
| C(7)-C(8)-H(8C) | 109.5 |
| H(8A)-C(8)-H(8C) | 109.5 |
| H(8B)-C(8)-H(8C) | 109.5 |
| O(3)-C(9)-C(10) | 111.4(3) |
| O(3)-C(9)-C(5) | 105.5(3) |
| C(10)-C(9)-C(5) | 115.2(3) |
| O(3)-C(9)-H(9) | 108.2 |
| C(10)-C(9)-H(9) | 108.2 |
| C(5)-C(9)-H(9) | 108.2 |
| C(11)-C(10)-C(15) | 117.8(3) |
| C(11)-C(10)-C(9) | 122.0(3) |
| C(15)-C(10)-C(9) | 120.1(3) |
| C(10)-C(11)-C(12) | 121.7(4) |
| C(10)-C(11)-H(11) | 119.1 |
| C(12)-C(11)-H(11) | 119.1 |
| C(13)-C(12)-C(11) | 119.3(4) |
| C(13)-C(12)-H(12) | 120.3 |
| C(11)-C(12)-H(12) | 120.3 |
| C(14)-C(13)-C(12) | 120.5(4) |
| C(14)-C(13)-H(13) | 119.8 |
| C(12)-C(13)-H(13) | 119.8 |
| C(13)-C(14)-C(15) | 120.7(4) |

| | |
|---|---|
| C(13)-C(14)-H(14) | 119.6 |
| C(15)-C(14)-H(14) | 119.6 |
| C(14)-C(15)-C(10) | 120.0(4) |
| C(14)-C(15)-H(15) | 120.0 |
| C(10)-C(15)-H(15) | 120.0 |
| O(4)-C(16)-O(5) | 116.6(3) |
| O(4)-C(16)-C(20) | 121.3(3) |
| O(5)-C(16)-C(20) | 122.1(3) |
| O(5)-C(17)-C(18) | 112.6(3) |
| O(5)-C(17)-H(17A) | 109.1 |
| C(18)-C(17)-H(17A) | 109.1 |
| O(5)-C(17)-H(17B) | 109.1 |
| C(18)-C(17)-H(17B) | 109.1 |
| H(17A)-C(17)-H(17B) | 107.8 |
| C(17)-C(18)-C(19) | 108.3(3) |
| C(17)-C(18)-H(18A) | 110.0 |
| C(19)-C(18)-H(18A) | 110.0 |
| C(17)-C(18)-H(18B) | 110.0 |
| C(19)-C(18)-H(18B) | 110.0 |
| H(18A)-C(18)-H(18B) | 108.4 |
| C(18)-C(19)-C(20) | 111.5(3) |
| C(18)-C(19)-H(19A) | 109.3 |
| C(20)-C(19)-H(19A) | 109.3 |
| C(18)-C(19)-H(19B) | 109.3 |
| C(20)-C(19)-H(19B) | 109.3 |
| H(19A)-C(19)-H(19B) | 108.0 |
| C(19)-C(20)-C(16) | 111.7(3) |
| C(19)-C(20)-C(24) | 111.5(3) |
| C(16)-C(20)-C(24) | 104.3(2) |
| C(19)-C(20)-C(21) | 108.9(3) |
| C(16)-C(20)-C(21) | 108.9(3) |
| C(24)-C(20)-C(21) | 111.4(3) |
| C(22)-C(21)-C(20) | 120.8(3) |
| C(22)-C(21)-H(21A) | 107.1 |
| C(20)-C(21)-H(21A) | 107.1 |
| C(22)-C(21)-H(21B) | 107.1 |
| C(20)-C(21)-H(21B) | 107.1 |
| H(21A)-C(21)-H(21B) | 106.8 |
| C(23)-C(22)-C(21) | 112.3(4) |
| C(23)-C(22)-H(22A) | 109.1 |
| C(21)-C(22)-H(22A) | 109.1 |
| C(23)-C(22)-H(22B) | 109.1 |
| C(21)-C(22)-H(22B) | 109.1 |
| H(22A)-C(22)-H(22B) | 107.9 |
| C(22)-C(23)-H(23A) | 109.5 |
| C(22)-C(23)-H(23B) | 109.5 |

| | |
|---|---|
| H(23A)-C(23)-H(23B) | 109.5 |
| C(22)-C(23)-H(23C) | 109.5 |
| H(23A)-C(23)-H(23C) | 109.5 |
| H(23B)-C(23)-H(23C) | 109.5 |
| O(6)-C(24)-C(25) | 110.8(3) |
| O(6)-C(24)-C(20) | 106.1(3) |
| C(25)-C(24)-C(20) | 115.0(3) |
| O(6)-C(24)-H(24) | 108.3 |
| C(25)-C(24)-H(24) | 108.3 |
| C(20)-C(24)-H(24) | 108.3 |
| C(30)-C(25)-C(26) | 117.8(3) |
| C(30)-C(25)-C(24) | 121.4(3) |
| C(26)-C(25)-C(24) | 120.8(3) |
| C(27)-C(26)-C(25) | 120.6(4) |
| C(27)-C(26)-H(26) | 119.7 |
| C(25)-C(26)-H(26) | 119.7 |
| C(28)-C(27)-C(26) | 120.2(4) |
| C(28)-C(27)-H(27) | 119.9 |
| C(26)-C(27)-H(27) | 119.9 |
| C(27)-C(28)-C(29) | 120.5(4) |
| C(27)-C(28)-H(28) | 119.7 |
| C(29)-C(28)-H(28) | 119.7 |
| C(28)-C(29)-C(30) | 119.5(4) |
| C(28)-C(29)-H(29) | 120.3 |
| C(30)-C(29)-H(29) | 120.3 |
| C(29)-C(30)-C(25) | 121.4(3) |
| C(29)-C(30)-H(30) | 119.3 |
| C(25)-C(30)-H(30) | 119.3 |

Table C.4d Anisotropic displacement parameters (A^2 x 10^3) for ydp3945. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| O(1) | 64(2) | 44(1) | 42(2) | 11(1) | 10(1) | 0(1) |
| O(2) | 54(1) | 54(2) | 49(2) | 7(1) | -2(1) | -13(1) |
| O(3) | 48(1) | 35(1) | 57(2) | -9(1) | 3(1) | 7(1) |
| O(4) | 67(2) | 41(1) | 43(2) | 10(1) | 14(1) | -2(1) |
| O(5) | 56(2) | 53(2) | 57(2) | 11(1) | 24(1) | 9(1) |
| O(6) | 48(1) | 35(1) | 58(2) | -11(1) | 16(1) | -8(1) |
| C(1) | 51(2) | 30(2) | 36(2) | 1(1) | 8(1) | 0(1) |
| C(2) | 55(2) | 50(2) | 56(2) | 8(2) | 8(2) | -12(2) |
| C(3) | 57(2) | 34(2) | 51(2) | 2(1) | 12(2) | -9(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(4) | 55(2) | 32(2) | 42(2) | 2(1) | 12(2) | -5(1) |
| C(5) | 48(2) | 29(2) | 34(2) | 2(1) | 5(1) | -1(1) |
| C(6) | 50(2) | 34(2) | 47(2) | 0(1) | 9(2) | 6(1) |
| C(7) | 57(2) | 53(2) | 70(3) | 8(2) | 24(2) | 10(2) |
| C(8) | 65(3) | 78(3) | 110(5) | 18(3) | 37(3) | 23(2) |
| C(9) | 45(2) | 30(2) | 38(2) | 2(1) | 8(1) | 3(1) |
| C(10) | 48(2) | 29(2) | 41(2) | -1(1) | 2(1) | -1(1) |
| C(11) | 55(2) | 37(2) | 47(2) | 1(1) | 8(2) | 2(2) |
| C(12) | 84(3) | 38(2) | 41(2) | 0(2) | 8(2) | 12(2) |
| C(13) | 74(3) | 53(2) | 51(3) | -7(2) | -10(2) | 11(2) |
| C(14) | 53(2) | 62(3) | 68(3) | 2(2) | -7(2) | 2(2) |
| C(15) | 47(2) | 54(2) | 56(2) | 0(2) | 5(2) | -4(2) |
| C(16) | 47(2) | 34(2) | 37(2) | 1(1) | 11(1) | -2(1) |
| C(17) | 52(2) | 50(2) | 59(2) | 12(2) | 17(2) | 10(2) |
| C(18) | 55(2) | 36(2) | 49(2) | 0(1) | 10(2) | 6(2) |
| C(19) | 57(2) | 33(2) | 39(2) | 2(1) | 14(2) | 5(1) |
| C(20) | 48(2) | 26(1) | 36(2) | 1(1) | 11(1) | -2(1) |
| C(21) | 53(2) | 33(2) | 42(2) | -3(1) | 12(2) | -6(1) |
| C(22) | 61(2) | 54(2) | 55(3) | 4(2) | 1(2) | -10(2) |
| C(23) | 57(2) | 77(3) | 74(3) | -1(2) | -3(2) | -15(2) |
| C(24) | 43(2) | 32(2) | 38(2) | 1(1) | 9(1) | -1(1) |
| C(25) | 42(2) | 29(2) | 43(2) | 1(1) | 10(1) | 1(1) |
| C(26) | 46(2) | 51(2) | 49(2) | 5(2) | 10(2) | 2(2) |
| C(27) | 45(2) | 63(3) | 69(3) | 2(2) | 18(2) | 3(2) |
| C(28) | 61(2) | 47(2) | 58(2) | -1(2) | 29(2) | -1(2) |
| C(29) | 65(2) | 43(2) | 40(2) | 1(2) | 16(2) | -2(2) |
| C(30) | 49(2) | 36(2) | 41(2) | -3(1) | 12(2) | 0(1) |

Table C.5d Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for ydp3945.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(3) | 3560(30) | -10(80) | 4360(60) | 82(17) |
| H(6) | 6400(40) | 4940(90) | 5200(70) | 89(18) |
| H(2A) | 5253 | 3553 | 6439 | 65 |
| H(2B) | 5229 | 4764 | 7627 | 65 |
| H(3A) | 4554 | 5604 | 5300 | 57 |
| H(3B) | 3880 | 5592 | 6352 | 57 |
| H(4A) | 4034 | 3304 | 4383 | 51 |
| H(4B) | 3275 | 4474 | 4104 | 51 |
| H(6A) | 2513 | 4793 | 6224 | 52 |
| H(6B) | 1955 | 3961 | 4892 | 52 |

| | | | | |
|---|---|---|---|---|
| H(7A) | 1577 | 2224 | 6569 | 70 |
| H(7B) | 2040 | 3261 | 7840 | 70 |
| H(8A) | 1049 | 5150 | 6868 | 122 |
| H(8B) | 560 | 3787 | 7356 | 122 |
| H(8C) | 562 | 4036 | 5694 | 122 |
| H(9) | 2547 | 907 | 5480 | 45 |
| H(11) | 3288 | 1965 | 2299 | 56 |
| H(12) | 2431 | 2082 | -19 | 66 |
| H(13) | 939 | 1800 | -342 | 75 |
| H(14) | 301 | 1416 | 1619 | 77 |
| H(15) | 1142 | 1324 | 3951 | 64 |
| H(17A) | 4794 | 9744 | 7551 | 63 |
| H(17B) | 4744 | 8545 | 6328 | 63 |
| H(18A) | 6117 | 10574 | 7126 | 56 |
| H(18B) | 5422 | 10586 | 5642 | 56 |
| H(19A) | 6697 | 9475 | 5251 | 51 |
| H(19B) | 5941 | 8299 | 5032 | 51 |
| H(21A) | 8024 | 9018 | 6907 | 51 |
| H(21B) | 7490 | 9752 | 7958 | 51 |
| H(22A) | 8016 | 8062 | 9750 | 70 |
| H(22B) | 8510 | 7223 | 8689 | 70 |
| H(23A) | 9405 | 9268 | 8635 | 107 |
| H(23B) | 9490 | 8698 | 10243 | 107 |
| H(23C) | 8917 | 10091 | 9713 | 107 |
| H(24) | 7454 | 5906 | 7075 | 45 |
| H(26) | 8827 | 6228 | 6387 | 58 |
| H(27) | 9630 | 6376 | 4567 | 69 |
| H(28) | 8947 | 6907 | 2222 | 64 |
| H(29) | 7452 | 7237 | 1639 | 58 |
| H(30) | 6640 | 7052 | 3435 | 50 |

Table C.6d Torsion angles [deg] for ydp3945.

| | |
|---|---|
| C(2)-O(2)-C(1)-O(1) | 177.2(3) |
| C(2)-O(2)-C(1)-C(5) | -4.4(5) |
| C(1)-O(2)-C(2)-C(3) | 28.7(5) |
| O(2)-C(2)-C(3)-C(4) | -56.6(4) |
| C(2)-C(3)-C(4)-C(5) | 62.3(4) |
| O(1)-C(1)-C(5)-C(6) | 67.6(4) |
| O(2)-C(1)-C(5)-C(6) | -110.7(4) |
| O(1)-C(1)-C(5)-C(9) | -52.1(4) |
| O(2)-C(1)-C(5)-C(9) | 129.6(3) |
| O(1)-C(1)-C(5)-C(4) | -172.7(3) |
| O(2)-C(1)-C(5)-C(4) | 9.0(4) |

| | |
|---|---|
| C(3)-C(4)-C(5)-C(6) | 82.5(4) |
| C(3)-C(4)-C(5)-C(1) | -38.3(4) |
| C(3)-C(4)-C(5)-C(9) | -154.8(3) |
| C(1)-C(5)-C(6)-C(7) | -49.0(4) |
| C(9)-C(5)-C(6)-C(7) | 66.4(4) |
| C(4)-C(5)-C(6)-C(7) | -170.9(3) |
| C(5)-C(6)-C(7)-C(8) | -171.3(4) |
| C(6)-C(5)-C(9)-O(3) | -177.1(3) |
| C(1)-C(5)-C(9)-O(3) | -58.6(3) |
| C(4)-C(5)-C(9)-O(3) | 62.2(3) |
| C(6)-C(5)-C(9)-C(10) | 59.7(4) |
| C(1)-C(5)-C(9)-C(10) | 178.1(3) |
| C(4)-C(5)-C(9)-C(10) | -61.1(4) |
| O(3)-C(9)-C(10)-C(11) | -34.7(4) |
| C(5)-C(9)-C(10)-C(11) | 85.4(4) |
| O(3)-C(9)-C(10)-C(15) | 142.4(3) |
| C(5)-C(9)-C(10)-C(15) | -97.6(4) |
| C(15)-C(10)-C(11)-C(12) | 0.3(5) |
| C(9)-C(10)-C(11)-C(12) | 177.4(3) |
| C(10)-C(11)-C(12)-C(13) | -0.4(6) |
| C(11)-C(12)-C(13)-C(14) | 0.2(6) |
| C(12)-C(13)-C(14)-C(15) | 0.3(7) |
| C(13)-C(14)-C(15)-C(10) | -0.4(7) |
| C(11)-C(10)-C(15)-C(14) | 0.2(6) |
| C(9)-C(10)-C(15)-C(14) | -177.0(4) |
| C(17)-O(5)-C(16)-O(4) | -177.5(3) |
| C(17)-O(5)-C(16)-C(20) | 4.3(5) |
| C(16)-O(5)-C(17)-C(18) | -28.2(5) |
| O(5)-C(17)-C(18)-C(19) | 56.0(4) |
| C(17)-C(18)-C(19)-C(20) | -61.9(4) |
| C(18)-C(19)-C(20)-C(16) | 38.3(4) |
| C(18)-C(19)-C(20)-C(24) | 154.6(3) |
| C(18)-C(19)-C(20)-C(21) | -82.0(3) |
| O(4)-C(16)-C(20)-C(19) | 172.4(3) |
| O(5)-C(16)-C(20)-C(19) | -9.5(4) |
| O(4)-C(16)-C(20)-C(24) | 51.8(4) |
| O(5)-C(16)-C(20)-C(24) | -130.1(3) |
| O(4)-C(16)-C(20)-C(21) | -67.2(4) |
| O(5)-C(16)-C(20)-C(21) | 110.8(4) |
| C(19)-C(20)-C(21)-C(22) | 174.4(3) |
| C(16)-C(20)-C(21)-C(22) | 52.4(4) |
| C(24)-C(20)-C(21)-C(22) | -62.2(4) |
| C(20)-C(21)-C(22)-C(23) | 175.9(4) |
| C(19)-C(20)-C(24)-O(6) | -62.3(3) |
| C(16)-C(20)-C(24)-O(6) | 58.5(3) |
| C(21)-C(20)-C(24)-O(6) | 175.8(3) |

| | |
|---|---|
| C(19)-C(20)-C(24)-C(25) | 60.6(4) |
| C(16)-C(20)-C(24)-C(25) | -178.7(3) |
| C(21)-C(20)-C(24)-C(25) | -61.4(4) |
| O(6)-C(24)-C(25)-C(30) | 37.4(4) |
| C(20)-C(24)-C(25)-C(30) | -82.8(4) |
| O(6)-C(24)-C(25)-C(26) | -139.2(3) |
| C(20)-C(24)-C(25)-C(26) | 100.6(4) |
| C(30)-C(25)-C(26)-C(27) | 1.0(5) |
| C(24)-C(25)-C(26)-C(27) | 177.7(3) |
| C(25)-C(26)-C(27)-C(28) | 0.3(6) |
| C(26)-C(27)-C(28)-C(29) | -1.0(6) |
| C(27)-C(28)-C(29)-C(30) | 0.4(6) |
| C(28)-C(29)-C(30)-C(25) | 0.9(5) |
| C(26)-C(25)-C(30)-C(29) | -1.6(5) |
| C(24)-C(25)-C(30)-C(29) | -178.3(3) |

Table C.7d Hydrogen bonds for ydp3945 [A and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(3)-H(3)...O(1)#1 | 0.87(7) | 1.99(7) | 2.850(4) | 171(6) |
| O(6)-H(6)...O(4)#2 | 0.93(8) | 1.89(7) | 2.820(4) | 174(6) |

Symmetry transformations used to generate equivalent atoms:
#1 x,-y,z-1/2 #2 x,-y+1,z-1/2

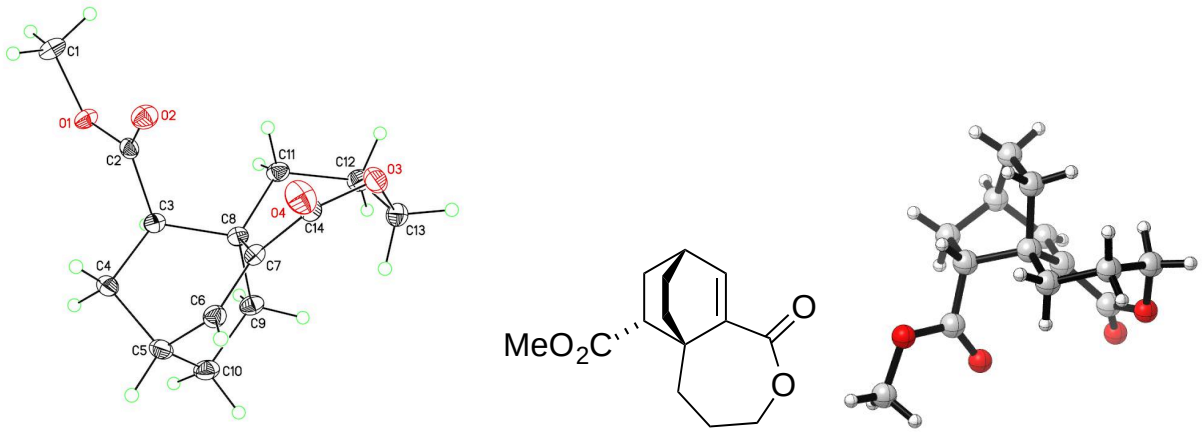



Figure C.5 Structure of fda.

**Structure Determination.**

Colorless plates of **fda** were grown from a dichloromethane/diethyl ether solution of the compound at 25 deg. C. A crystal of dimensions 0.12 x 0.10 x 0.08 mm was mounted on a

Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (ë = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ù. The exposure times were 1 sec. for the low angle images, 6 sec. for high angle. The integration of the data yielded a total of 17889 reflections to a maximum 2è value of 136.48° of which 2178 were independent and 2042 were greater than 2ó(I). The final cell constants (Table 1) were based on the xyz centroids 11562 reflections above 10ó(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package, using the space group P2(1)/c with Z = 4 for the formula $C_{14}H_{18}O_4$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on $F^2$ converged at R1 = 0.0336 and wR2 = 0.0836 [based on I > 2sigma(I)], R1 = 0.0353 and wR2 = 0.0850 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Table C.1e Crystal data and structure refinement for fda.

| | |
|---|---|
| Identification code | fda |
| Empirical formula | C14 H18 O4 |
| Formula weight | 250.28 |
| Temperature | 85(2) K |
| Wavelength | 1.54178 A |
| Crystal system, space group | Monoclinic, P2(1)/c |
| Unit cell dimensions | a = 13.0061(9) A alpha = 90 deg. |
| | b = 8.6951(2) A beta = 109.666(8) deg. |
| | c = 11.2164(2) A gamma = 90 deg. |
| Volume | 1194.47(9) A^3 |
| Z, Calculated density | 4, 1.392 Mg/m^3 |
| Absorption coefficient | 0.833 mm^-1 |
| F(000) | 536 |
| Crystal size | 0.12 x 0.10 x 0.03 mm |
| Theta range for data collection | 3.61 to 68.24 deg. |
| Limiting indices | -15<=h<=15, -10<=k<=10, -13<=l<=13 |
| Reflections collected / unique | 17889 / 2178 [R(int) = 0.0480] |
| Completeness to theta = 68.24 | 99.8 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9755 and 0.9067 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 2178 / 0 / 165 |
| Goodness-of-fit on F^2 | 1.059 |
| Final R indices [I>2sigma(I)] | R1 = 0.0336, wR2 = 0.0836 |
| R indices (all data) | R1 = 0.0353, wR2 = 0.0850 |
| Extinction coefficient | 0.0034(5) |

Largest diff. peak and hole 0.244 and -0.171 e.A^-3

Table C.2e Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for fda. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 5899(1) | 990(1) | 6270(1) | 17(1) |
| O(2) | 6535(1) | 2604(1) | 7922(1) | 20(1) |
| O(3) | 7305(1) | 7208(1) | 7828(1) | 20(1) |
| O(4) | 8164(1) | 5867(1) | 9537(1) | 25(1) |
| C(1) | 5138(1) | 367(2) | 6840(1) | 22(1) |
| C(2) | 6576(1) | 2095(1) | 6936(1) | 14(1) |
| C(3) | 7388(1) | 2546(1) | 6300(1) | 15(1) |
| C(4) | 8498(1) | 1728(1) | 6967(1) | 18(1) |
| C(5) | 9421(1) | 2928(1) | 7226(1) | 18(1) |
| C(6) | 9210(1) | 4126(1) | 8074(1) | 16(1) |
| C(7) | 8243(1) | 4836(1) | 7608(1) | 14(1) |
| C(8) | 7554(1) | 4324(1) | 6280(1) | 14(1) |
| C(9) | 8254(1) | 4553(2) | 5409(1) | 17(1) |
| C(10) | 9348(1) | 3678(2) | 5953(1) | 20(1) |
| C(11) | 6434(1) | 5096(1) | 5750(1) | 17(1) |
| C(12) | 6458(1) | 6827(2) | 5520(1) | 20(1) |
| C(13) | 7319(1) | 7649(1) | 6580(1) | 19(1) |
| C(14) | 7914(1) | 5979(1) | 8400(1) | 16(1) |

Table C.3e Bond lengths [A] and angles [deg] for fda.

| | |
|---|---|
| O(1)-C(2) | 1.3463(14) |
| O(1)-C(1) | 1.4513(14) |
| O(2)-C(2) | 1.2088(15) |
| O(3)-C(14) | 1.3560(15) |
| O(3)-C(13) | 1.4567(15) |
| O(4)-C(14) | 1.2092(15) |
| C(1)-H(1A) | 0.9800 |
| C(1)-H(1B) | 0.9800 |
| C(1)-H(1C) | 0.9800 |
| C(2)-C(3) | 1.5125(16) |
| C(3)-C(4) | 1.5561(16) |
| C(3)-C(8) | 1.5621(16) |
| C(3)-H(3) | 1.0000 |
| C(4)-C(5) | 1.5427(16) |

| | |
|---|---|
| C(4)-H(4A) | 0.9900 |
| C(4)-H(4B) | 0.9900 |
| C(5)-C(6) | 1.4961(17) |
| C(5)-C(10) | 1.5436(17) |
| C(5)-H(5) | 1.0000 |
| C(6)-C(7) | 1.3391(17) |
| C(6)-H(6) | 0.9500 |
| C(7)-C(14) | 1.4886(16) |
| C(7)-C(8) | 1.5239(15) |
| C(8)-C(11) | 1.5303(16) |
| C(8)-C(9) | 1.5563(16) |
| C(9)-C(10) | 1.5476(17) |
| C(9)-H(9A) | 0.9900 |
| C(9)-H(9B) | 0.9900 |
| C(10)-H(10A) | 0.9900 |
| C(10)-H(10B) | 0.9900 |
| C(11)-C(12) | 1.5287(17) |
| C(11)-H(11A) | 0.9900 |
| C(11)-H(11B) | 0.9900 |
| C(12)-C(13) | 1.5115(18) |
| C(12)-H(12A) | 0.9900 |
| C(12)-H(12B) | 0.9900 |
| C(13)-H(13A) | 0.9900 |
| C(13)-H(13B) | 0.9900 |
| C(2)-O(1)-C(1) | 115.94(9) |
| C(14)-O(3)-C(13) | 117.94(9) |
| O(1)-C(1)-H(1A) | 109.5 |
| O(1)-C(1)-H(1B) | 109.5 |
| H(1A)-C(1)-H(1B) | 109.5 |
| O(1)-C(1)-H(1C) | 109.5 |
| H(1A)-C(1)-H(1C) | 109.5 |
| H(1B)-C(1)-H(1C) | 109.5 |
| O(2)-C(2)-O(1) | 123.15(10) |
| O(2)-C(2)-C(3) | 126.12(11) |
| O(1)-C(2)-C(3) | 110.70(9) |
| C(2)-C(3)-C(4) | 109.67(9) |
| C(2)-C(3)-C(8) | 112.62(9) |
| C(4)-C(3)-C(8) | 110.44(9) |
| C(2)-C(3)-H(3) | 108.0 |
| C(4)-C(3)-H(3) | 108.0 |
| C(8)-C(3)-H(3) | 108.0 |
| C(5)-C(4)-C(3) | 108.58(10) |
| C(5)-C(4)-H(4A) | 110.0 |
| C(3)-C(4)-H(4A) | 110.0 |
| C(5)-C(4)-H(4B) | 110.0 |
| C(3)-C(4)-H(4B) | 110.0 |

| | |
|---|---|
| H(4A)-C(4)-H(4B) | 108.4 |
| C(6)-C(5)-C(4) | 107.04(10) |
| C(6)-C(5)-C(10) | 109.07(10) |
| C(4)-C(5)-C(10) | 108.06(10) |
| C(6)-C(5)-H(5) | 110.8 |
| C(4)-C(5)-H(5) | 110.8 |
| C(10)-C(5)-H(5) | 110.8 |
| C(7)-C(6)-C(5) | 114.94(10) |
| C(7)-C(6)-H(6) | 122.5 |
| C(5)-C(6)-H(6) | 122.5 |
| C(6)-C(7)-C(14) | 119.72(10) |
| C(6)-C(7)-C(8) | 114.43(10) |
| C(14)-C(7)-C(8) | 125.82(10) |
| C(7)-C(8)-C(11) | 114.95(10) |
| C(7)-C(8)-C(9) | 107.46(9) |
| C(11)-C(8)-C(9) | 112.41(9) |
| C(7)-C(8)-C(3) | 108.27(9) |
| C(11)-C(8)-C(3) | 108.80(9) |
| C(9)-C(8)-C(3) | 104.35(9) |
| C(10)-C(9)-C(8) | 110.16(9) |
| C(10)-C(9)-H(9A) | 109.6 |
| C(8)-C(9)-H(9A) | 109.6 |
| C(10)-C(9)-H(9B) | 109.6 |
| C(8)-C(9)-H(9B) | 109.6 |
| H(9A)-C(9)-H(9B) | 108.1 |
| C(5)-C(10)-C(9) | 109.52(9) |
| C(5)-C(10)-H(10A) | 109.8 |
| C(9)-C(10)-H(10A) | 109.8 |
| C(5)-C(10)-H(10B) | 109.8 |
| C(9)-C(10)-H(10B) | 109.8 |
| H(10A)-C(10)-H(10B) | 108.2 |
| C(12)-C(11)-C(8) | 115.27(10) |
| C(12)-C(11)-H(11A) | 108.5 |
| C(8)-C(11)-H(11A) | 108.5 |
| C(12)-C(11)-H(11B) | 108.5 |
| C(8)-C(11)-H(11B) | 108.5 |
| H(11A)-C(11)-H(11B) | 107.5 |
| C(13)-C(12)-C(11) | 112.62(10) |
| C(13)-C(12)-H(12A) | 109.1 |
| C(11)-C(12)-H(12A) | 109.1 |
| C(13)-C(12)-H(12B) | 109.1 |
| C(11)-C(12)-H(12B) | 109.1 |
| H(12A)-C(12)-H(12B) | 107.8 |
| O(3)-C(13)-C(12) | 112.65(10) |
| O(3)-C(13)-H(13A) | 109.1 |
| C(12)-C(13)-H(13A) | 109.1 |

| | |
|---|---|
| O(3)-C(13)-H(13B) | 109.1 |
| C(12)-C(13)-H(13B) | 109.1 |
| H(13A)-C(13)-H(13B) | 107.8 |
| O(4)-C(14)-O(3) | 118.01(11) |
| O(4)-C(14)-C(7) | 123.13(11) |
| O(3)-C(14)-C(7) | 118.87(10) |

Table C.4e Anisotropic displacement parameters (A^2 x 10^3) for fda.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| O(1) | 15(1) | 18(1) | 19(1) | -2(1) | 7(1) | -5(1) |
| O(2) | 21(1) | 22(1) | 18(1) | -2(1) | 9(1) | -2(1) |
| O(3) | 22(1) | 17(1) | 22(1) | 1(1) | 9(1) | 4(1) |
| O(4) | 31(1) | 26(1) | 17(1) | -2(1) | 9(1) | 4(1) |
| C(1) | 19(1) | 25(1) | 24(1) | 1(1) | 11(1) | -7(1) |
| C(2) | 12(1) | 13(1) | 15(1) | 2(1) | 2(1) | 2(1) |
| C(3) | 14(1) | 16(1) | 14(1) | -3(1) | 6(1) | -2(1) |
| C(4) | 15(1) | 15(1) | 24(1) | -2(1) | 8(1) | 1(1) |
| C(5) | 12(1) | 18(1) | 23(1) | -2(1) | 6(1) | 1(1) |
| C(6) | 14(1) | 16(1) | 16(1) | 0(1) | 4(1) | -2(1) |
| C(7) | 14(1) | 14(1) | 14(1) | 0(1) | 5(1) | -2(1) |
| C(8) | 13(1) | 15(1) | 13(1) | 0(1) | 4(1) | -1(1) |
| C(9) | 16(1) | 22(1) | 15(1) | -2(1) | 7(1) | -4(1) |
| C(10) | 17(1) | 23(1) | 24(1) | -5(1) | 12(1) | -3(1) |
| C(11) | 12(1) | 20(1) | 17(1) | 3(1) | 4(1) | 0(1) |
| C(12) | 15(1) | 21(1) | 23(1) | 7(1) | 4(1) | 2(1) |
| C(13) | 19(1) | 16(1) | 24(1) | 5(1) | 8(1) | 1(1) |
| C(14) | 15(1) | 15(1) | 19(1) | -1(1) | 6(1) | 0(1) |

Table C.5e Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for fda.

| | x | y | z | U(eq) |
|---|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| H(1A) | 5540 | -230 | 7594 | 33 |
| H(1B) | 4612 | -301 | 6229 | 33 |
| H(1C) | 4750 | 1212 | 7082 | 33 |
| H(3) | 7102 | 2178 | 5403 | 18 |
| H(4A) | 8499 | 1265 | 7774 | 22 |
| H(4B) | 8610 | 898 | 6420 | 22 |
| H(5) | 10151 | 2437 | 7634 | 21 |
| H(6) | 9724 | 4365 | 8882 | 19 |
| H(9A) | 7847 | 4167 | 4548 | 21 |
| H(9B) | 8398 | 5662 | 5344 | 21 |
| H(10A) | 9397 | 2875 | 5348 | 24 |
| H(10B) | 9965 | 4400 | 6082 | 24 |
| H(11A) | 6018 | 4593 | 4939 | 20 |
| H(11B) | 6032 | 4914 | 6346 | 20 |
| H(12A) | 6599 | 7004 | 4717 | 24 |
| H(12B) | 5733 | 7268 | 5428 | 24 |
| H(13A) | 8048 | 7417 | 6526 | 23 |
| H(13B) | 7201 | 8773 | 6472 | 23 |

Table C.6e Torsion angles [deg] for fda.

| | |
|---|---|
| C(1)-O(1)-C(2)-O(2) | -3.18(16) |
| C(1)-O(1)-C(2)-C(3) | 175.04(10) |
| O(2)-C(2)-C(3)-C(4) | 78.42(14) |
| O(1)-C(2)-C(3)-C(4) | -99.73(11) |
| O(2)-C(2)-C(3)-C(8) | -45.00(16) |
| O(1)-C(2)-C(3)-C(8) | 136.84(10) |
| C(2)-C(3)-C(4)-C(5) | -132.44(10) |
| C(8)-C(3)-C(4)-C(5) | -7.75(13) |
| C(3)-C(4)-C(5)-C(6) | 60.66(12) |
| C(3)-C(4)-C(5)-C(10) | -56.70(12) |
| C(4)-C(5)-C(6)-C(7) | -58.38(13) |
| C(10)-C(5)-C(6)-C(7) | 58.31(13) |
| C(5)-C(6)-C(7)-C(14) | 176.15(10) |
| C(5)-C(6)-C(7)-C(8) | -1.91(15) |
| C(6)-C(7)-C(8)-C(11) | 178.49(10) |
| C(14)-C(7)-C(8)-C(11) | 0.57(16) |
| C(6)-C(7)-C(8)-C(9) | -55.56(13) |
| C(14)-C(7)-C(8)-C(9) | 126.52(12) |
| C(6)-C(7)-C(8)-C(3) | 56.62(13) |
| C(14)-C(7)-C(8)-C(3) | -121.30(12) |
| C(2)-C(3)-C(8)-C(7) | 74.71(12) |
| C(4)-C(3)-C(8)-C(7) | -48.28(12) |
| C(2)-C(3)-C(8)-C(11) | -50.86(12) |

| | |
|---|---|
| C(4)-C(3)-C(8)-C(11) | -173.85(9) |
| C(2)-C(3)-C(8)-C(9) | -171.04(9) |
| C(4)-C(3)-C(8)-C(9) | 65.97(11) |
| C(7)-C(8)-C(9)-C(10) | 55.56(12) |
| C(11)-C(8)-C(9)-C(10) | -176.99(10) |
| C(3)-C(8)-C(9)-C(10) | -59.26(12) |
| C(6)-C(5)-C(10)-C(9) | -52.54(13) |
| C(4)-C(5)-C(10)-C(9) | 63.49(12) |
| C(8)-C(9)-C(10)-C(5) | -3.01(14) |
| C(7)-C(8)-C(11)-C(12) | 65.41(13) |
| C(9)-C(8)-C(11)-C(12) | -57.95(13) |
| C(3)-C(8)-C(11)-C(12) | -173.01(10) |
| C(8)-C(11)-C(12)-C(13) | -42.13(14) |
| C(14)-O(3)-C(13)-C(12) | 88.56(12) |
| C(11)-C(12)-C(13)-O(3) | -47.36(14) |
| C(13)-O(3)-C(14)-O(4) | 158.99(11) |
| C(13)-O(3)-C(14)-C(7) | -20.98(15) |
| C(6)-C(7)-C(14)-O(4) | -33.96(18) |
| C(8)-C(7)-C(14)-O(4) | 143.86(12) |
| C(6)-C(7)-C(14)-O(3) | 146.00(11) |
| C(8)-C(7)-C(14)-O(3) | -36.18(17) |

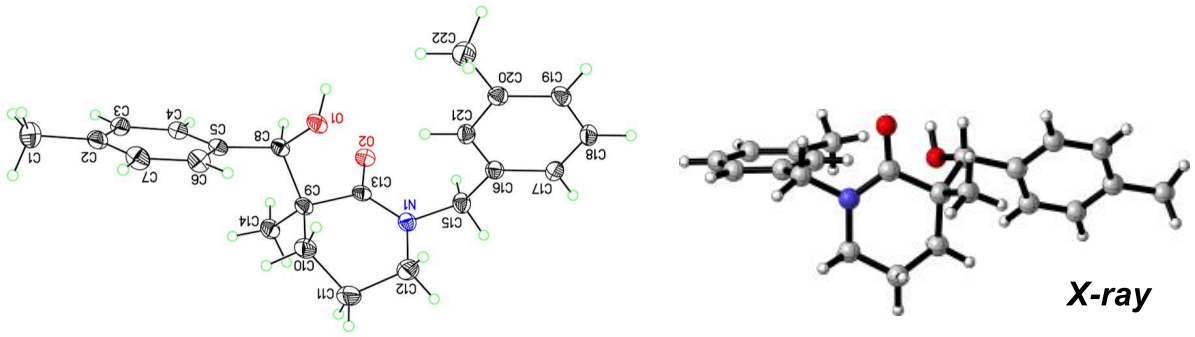



Figure C.6 Structure of ydp0201.

**Structure Determination.**

Colorless block-like crystals of **ydp0201** were grown from a dichloromethane/hexanes solution of the compound at 22 deg. C. A crystal of dimensions 0.24 x 0.08 x 0.08 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (ë = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ù. The exposure times were 1 sec. for the low angle images, 6 sec. for high angle. The integration of the data yielded a total of 27056 reflections to a maximum 2è value of 136.44° of which 3381 were independent and 3099 were greater than 2ó(I). The final cell constants (Table 1) were based on the xyz centroids 11215 reflections above 10ó(I). Analysis of the data showed negligible decay during data collection;

the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group P2(1)/c with Z = 4 for the formula $C_{22}H_{27}NO_2$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in both idealized and refined positions. Full matrix least-squares refinement based on $F^2$ converged at R1 = 0.0423 and wR2 = 0.1123 [based on I > 2sigma(I)], R1 = 0.0450 and wR2 = 0.1144 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Table C.1f Crystal data and structure refinement for ydp0201.

| | |
|---|---|
| Identification code | ydp0201 |
| Empirical formula | C22 H27 N O2 |
| Formula weight | 337.44 |
| Temperature | 85(2) K |
| Wavelength | 1.54178 A |
| Crystal system, space group | Monoclinic, P2(1)/c |
| Unit cell dimensions | a = 11.9334(2) A alpha = 90 deg.<br>b = 7.89830(10) A beta = 95.783(7) deg.<br>c = 19.6898(14) A gamma = 90 deg. |
| Volume | 1846.39(14) A^3 |
| Z, Calculated density | 4, 1.214 Mg/m^3 |
| Absorption coefficient | 0.601 mm^-1 |
| F(000) | 728 |
| Crystal size | 0.240 x 0.080 x 0.080 mm |
| Theta range for data collection | 3.723 to 68.218 deg. |
| Limiting indices | -14<=h<=14, -9<=k<=9, -20<=l<=23 |
| Reflections collected / unique | 27506 / 3381 [R(int) = 0.0664] |
| Completeness to theta = 67.679 | 99.8 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.953 and 0.800 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 3381 / 0 / 234 |
| Goodness-of-fit on F^2 | 1.064 |
| Final R indices [I>2sigma(I)] | R1 = 0.0423, wR2 = 0.1123 |
| R indices (all data) | R1 = 0.0450, wR2 = 0.1144 |
| Extinction coefficient | 0.0040(5) |
| Largest diff. peak and hole | 0.408 and -0.266 e.A^-3 |

Table C.2f Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for ydp0201. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| x | y | z | U(eq) |
|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| O(1) | 4667(1) | 4298(1) | 3858(1) | 21(1) |
| O(2) | 4533(1) | 7237(1) | 4951(1) | 22(1) |
| N(1) | 5198(1) | 8650(1) | 4081(1) | 20(1) |
| C(13) | 4460(1) | 7586(2) | 4336(1) | 18(1) |
| C(5) | 2658(1) | 3787(2) | 3665(1) | 18(1) |
| C(21) | 7153(1) | 6471(2) | 4162(1) | 19(1) |
| C(8) | 3584(1) | 4866(2) | 4026(1) | 18(1) |
| C(20) | 8102(1) | 5496(2) | 4074(1) | 20(1) |
| C(4) | 1768(1) | 3244(2) | 4016(1) | 20(1) |
| C(16) | 7246(1) | 8164(2) | 4357(1) | 19(1) |
| C(9) | 3500(1) | 6789(2) | 3858(1) | 20(1) |
| C(18) | 9263(1) | 7947(2) | 4365(1) | 23(1) |
| C(3) | 943(1) | 2171(2) | 3705(1) | 22(1) |
| C(19) | 9164(1) | 6252(2) | 4184(1) | 21(1) |
| C(17) | 8310(1) | 8905(2) | 4450(1) | 22(1) |
| C(2) | 970(1) | 1635(2) | 3037(1) | 24(1) |
| C(15) | 6215(1) | 9165(2) | 4510(1) | 22(1) |
| C(6) | 2689(1) | 3236(2) | 2996(1) | 24(1) |
| C(14) | 2383(1) | 7497(2) | 4066(1) | 25(1) |
| C(12) | 5152(1) | 9190(2) | 3370(1) | 29(1) |
| C(10) | 3622(1) | 7123(2) | 3103(1) | 26(1) |
| C(7) | 1854(1) | 2198(2) | 2684(1) | 26(1) |
| C(22) | 7971(1) | 3674(2) | 3857(1) | 29(1) |
| C(11) | 4004(1) | 8925(2) | 2990(1) | 31(1) |
| C(1) | 72(1) | 473(2) | 2705(1) | 34(1) |

Table C.3f Bond lengths [A] and angles [deg] for ydp0201.

| | |
|---|---|
| O(1)-C(8) | 1.4367(14) |
| O(1)-H(1) | 0.88(2) |
| O(2)-C(13) | 1.2357(16) |
| N(1)-C(13) | 1.3506(17) |
| N(1)-C(12) | 1.4586(19) |
| N(1)-C(15) | 1.4638(17) |
| C(13)-C(9) | 1.5424(18) |
| C(5)-C(6) | 1.391(2) |
| C(5)-C(4) | 1.3922(18) |
| C(5)-C(8) | 1.5149(17) |
| C(21)-C(16) | 1.3921(18) |
| C(21)-C(20) | 1.3940(18) |
| C(21)-H(21) | 0.9500 |
| C(8)-C(9) | 1.5556(17) |
| C(8)-H(8) | 1.0000 |
| C(20)-C(19) | 1.3986(18) |

| | |
|---|---|
| C(20)-C(22) | 1.5051(19) |
| C(4)-C(3) | 1.3927(19) |
| C(4)-H(4) | 0.9500 |
| C(16)-C(17) | 1.3939(18) |
| C(16)-C(15) | 1.5184(17) |
| C(9)-C(10) | 1.5323(19) |
| C(9)-C(14) | 1.5377(17) |
| C(18)-C(19) | 1.3878(19) |
| C(18)-C(17) | 1.3897(19) |
| C(18)-H(18) | 0.9500 |
| C(3)-C(2) | 1.386(2) |
| C(3)-H(3) | 0.9500 |
| C(19)-H(19) | 0.9500 |
| C(17)-H(17) | 0.9500 |
| C(2)-C(7) | 1.393(2) |
| C(2)-C(1) | 1.5087(19) |
| C(15)-H(15A) | 0.9900 |
| C(15)-H(15B) | 0.9900 |
| C(6)-C(7) | 1.385(2) |
| C(6)-H(6) | 0.9500 |
| C(14)-H(14A) | 0.9800 |
| C(14)-H(14B) | 0.9800 |
| C(14)-H(14C) | 0.9800 |
| C(12)-C(11) | 1.508(2) |
| C(12)-H(12A) | 0.9900 |
| C(12)-H(12B) | 0.9900 |
| C(10)-C(11) | 1.517(2) |
| C(10)-H(10A) | 0.9900 |
| C(10)-H(10B) | 0.9900 |
| C(7)-H(7) | 0.9500 |
| C(22)-H(22A) | 0.9800 |
| C(22)-H(22B) | 0.9800 |
| C(22)-H(22C) | 0.9800 |
| C(11)-H(11A) | 0.9900 |
| C(11)-H(11B) | 0.9900 |
| C(1)-H(1A) | 0.9800 |
| C(1)-H(1B) | 0.9800 |
| C(1)-H(1C) | 0.9800 |
| C(8)-O(1)-H(1) | 105.3(13) |
| C(13)-N(1)-C(12) | 125.19(11) |
| C(13)-N(1)-C(15) | 119.46(11) |
| C(12)-N(1)-C(15) | 114.88(11) |
| O(2)-C(13)-N(1) | 121.31(12) |
| O(2)-C(13)-C(9) | 118.76(11) |
| N(1)-C(13)-C(9) | 119.93(11) |
| C(6)-C(5)-C(4) | 117.87(12) |

| | |
|---|---|
| C(6)-C(5)-C(8) | 122.19(12) |
| C(4)-C(5)-C(8) | 119.86(12) |
| C(16)-C(21)-C(20) | 121.47(12) |
| C(16)-C(21)-H(21) | 119.3 |
| C(20)-C(21)-H(21) | 119.3 |
| O(1)-C(8)-C(5) | 110.30(10) |
| O(1)-C(8)-C(9) | 107.28(10) |
| C(5)-C(8)-C(9) | 114.89(10) |
| O(1)-C(8)-H(8) | 108.1 |
| C(5)-C(8)-H(8) | 108.1 |
| C(9)-C(8)-H(8) | 108.1 |
| C(21)-C(20)-C(19) | 118.64(12) |
| C(21)-C(20)-C(22) | 120.13(12) |
| C(19)-C(20)-C(22) | 121.23(12) |
| C(5)-C(4)-C(3) | 120.70(13) |
| C(5)-C(4)-H(4) | 119.7 |
| C(3)-C(4)-H(4) | 119.7 |
| C(21)-C(16)-C(17) | 119.05(12) |
| C(21)-C(16)-C(15) | 120.76(11) |
| C(17)-C(16)-C(15) | 120.08(11) |
| C(10)-C(9)-C(14) | 111.43(11) |
| C(10)-C(9)-C(13) | 112.62(11) |
| C(14)-C(9)-C(13) | 107.44(10) |
| C(10)-C(9)-C(8) | 111.33(11) |
| C(14)-C(9)-C(8) | 109.76(10) |
| C(13)-C(9)-C(8) | 103.93(9) |
| C(19)-C(18)-C(17) | 120.43(12) |
| C(19)-C(18)-H(18) | 119.8 |
| C(17)-C(18)-H(18) | 119.8 |
| C(2)-C(3)-C(4) | 121.33(13) |
| C(2)-C(3)-H(3) | 119.3 |
| C(4)-C(3)-H(3) | 119.3 |
| C(18)-C(19)-C(20) | 120.28(12) |
| C(18)-C(19)-H(19) | 119.9 |
| C(20)-C(19)-H(19) | 119.9 |
| C(18)-C(17)-C(16) | 120.09(12) |
| C(18)-C(17)-H(17) | 120.0 |
| C(16)-C(17)-H(17) | 120.0 |
| C(3)-C(2)-C(7) | 117.79(12) |
| C(3)-C(2)-C(1) | 120.87(13) |
| C(7)-C(2)-C(1) | 121.34(13) |
| N(1)-C(15)-C(16) | 112.46(11) |
| N(1)-C(15)-H(15A) | 109.1 |
| C(16)-C(15)-H(15A) | 109.1 |
| N(1)-C(15)-H(15B) | 109.1 |
| C(16)-C(15)-H(15B) | 109.1 |

| | |
|---|---|
| H(15A)-C(15)-H(15B) | 107.8 |
| C(7)-C(6)-C(5) | 121.22(13) |
| C(7)-C(6)-H(6) | 119.4 |
| C(5)-C(6)-H(6) | 119.4 |
| C(9)-C(14)-H(14A) | 109.5 |
| C(9)-C(14)-H(14B) | 109.5 |
| H(14A)-C(14)-H(14B) | 109.5 |
| C(9)-C(14)-H(14C) | 109.5 |
| H(14A)-C(14)-H(14C) | 109.5 |
| H(14B)-C(14)-H(14C) | 109.5 |
| N(1)-C(12)-C(11) | 112.36(12) |
| N(1)-C(12)-H(12A) | 109.1 |
| C(11)-C(12)-H(12A) | 109.1 |
| N(1)-C(12)-H(12B) | 109.1 |
| C(11)-C(12)-H(12B) | 109.1 |
| H(12A)-C(12)-H(12B) | 107.9 |
| C(11)-C(10)-C(9) | 111.30(12) |
| C(11)-C(10)-H(10A) | 109.4 |
| C(9)-C(10)-H(10A) | 109.4 |
| C(11)-C(10)-H(10B) | 109.4 |
| C(9)-C(10)-H(10B) | 109.4 |
| H(10A)-C(10)-H(10B) | 108.0 |
| C(6)-C(7)-C(2) | 121.05(13) |
| C(6)-C(7)-H(7) | 119.5 |
| C(2)-C(7)-H(7) | 119.5 |
| C(20)-C(22)-H(22A) | 109.5 |
| C(20)-C(22)-H(22B) | 109.5 |
| H(22A)-C(22)-H(22B) | 109.5 |
| C(20)-C(22)-H(22C) | 109.5 |
| H(22A)-C(22)-H(22C) | 109.5 |
| H(22B)-C(22)-H(22C) | 109.5 |
| C(12)-C(11)-C(10) | 109.17(12) |
| C(12)-C(11)-H(11A) | 109.8 |
| C(10)-C(11)-H(11A) | 109.8 |
| C(12)-C(11)-H(11B) | 109.8 |
| C(10)-C(11)-H(11B) | 109.8 |
| H(11A)-C(11)-H(11B) | 108.3 |
| C(2)-C(1)-H(1A) | 109.5 |
| C(2)-C(1)-H(1B) | 109.5 |
| H(1A)-C(1)-H(1B) | 109.5 |
| C(2)-C(1)-H(1C) | 109.5 |
| H(1A)-C(1)-H(1C) | 109.5 |
| H(1B)-C(1)-H(1C) | 109.5 |

Table C.4f Anisotropic displacement parameters (A^2 x 10^3) for ydp0201. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| O(1) | 15(1) | 26(1) | 22(1) | 2(1) | 4(1) | 6(1) |
| O(2) | 23(1) | 22(1) | 19(1) | 0(1) | 2(1) | 3(1) |
| N(1) | 16(1) | 22(1) | 23(1) | 1(1) | 4(1) | 3(1) |
| C(13) | 17(1) | 17(1) | 19(1) | 1(1) | 3(1) | 6(1) |
| C(5) | 17(1) | 19(1) | 19(1) | 1(1) | 0(1) | 4(1) |
| C(21) | 17(1) | 22(1) | 20(1) | 1(1) | 3(1) | -1(1) |
| C(8) | 15(1) | 22(1) | 17(1) | 1(1) | 4(1) | 4(1) |
| C(20) | 20(1) | 21(1) | 19(1) | 3(1) | 4(1) | 2(1) |
| C(4) | 21(1) | 21(1) | 19(1) | 1(1) | 1(1) | 3(1) |
| C(16) | 18(1) | 21(1) | 20(1) | 2(1) | 3(1) | 1(1) |
| C(9) | 16(1) | 22(1) | 20(1) | 2(1) | 2(1) | 3(1) |
| C(18) | 17(1) | 27(1) | 24(1) | 4(1) | 3(1) | -3(1) |
| C(3) | 20(1) | 21(1) | 24(1) | 3(1) | 2(1) | 1(1) |
| C(19) | 16(1) | 27(1) | 22(1) | 4(1) | 4(1) | 3(1) |
| C(17) | 21(1) | 20(1) | 25(1) | 1(1) | 3(1) | -2(1) |
| C(2) | 24(1) | 19(1) | 26(1) | -1(1) | -5(1) | 4(1) |
| C(15) | 18(1) | 21(1) | 28(1) | -4(1) | 3(1) | 1(1) |
| C(6) | 23(1) | 29(1) | 21(1) | -2(1) | 5(1) | 2(1) |
| C(14) | 17(1) | 24(1) | 34(1) | 0(1) | 2(1) | 5(1) |
| C(12) | 26(1) | 34(1) | 27(1) | 9(1) | 6(1) | -1(1) |
| C(10) | 27(1) | 30(1) | 20(1) | 4(1) | -1(1) | 0(1) |
| C(7) | 29(1) | 28(1) | 20(1) | -6(1) | 0(1) | 5(1) |
| C(22) | 26(1) | 23(1) | 39(1) | -2(1) | 8(1) | 2(1) |
| C(11) | 32(1) | 33(1) | 27(1) | 9(1) | 1(1) | 2(1) |
| C(1) | 37(1) | 31(1) | 33(1) | -4(1) | -7(1) | -6(1) |

Table C.5f Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for ydp0201.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 4960(16) | 3740(20) | 4221(11) | 38(5) |
| H(21) | 6428 | 5970 | 4087 | 23 |
| H(8) | 3560 | 4727 | 4529 | 22 |
| H(4) | 1723 | 3608 | 4472 | 24 |
| H(18) | 9987 | 8456 | 4432 | 27 |

| | | | | |
|---|---|---|---|---|
| H(3) | 350 | 1800 | 3956 | 26 |
| H(19) | 9821 | 5602 | 4134 | 26 |
| H(17) | 8385 | 10067 | 4571 | 26 |
| H(15A) | 6092 | 9007 | 4995 | 27 |
| H(15B) | 6353 | 10385 | 4436 | 27 |
| H(6) | 3294 | 3577 | 2749 | 29 |
| H(14A) | 2363 | 8726 | 3997 | 38 |
| H(14B) | 2323 | 7243 | 4548 | 38 |
| H(14C) | 1752 | 6974 | 3784 | 38 |
| H(12A) | 5717 | 8546 | 3140 | 34 |
| H(12B) | 5352 | 10405 | 3354 | 34 |
| H(10A) | 4178 | 6323 | 2942 | 31 |
| H(10B) | 2890 | 6924 | 2831 | 31 |
| H(7) | 1885 | 1865 | 2223 | 31 |
| H(22A) | 7199 | 3300 | 3903 | 43 |
| H(22B) | 8501 | 2972 | 4147 | 43 |
| H(22C) | 8128 | 3563 | 3380 | 43 |
| H(11A) | 4039 | 9130 | 2496 | 37 |
| H(11B) | 3460 | 9733 | 3156 | 37 |
| H(1A) | 427 | -461 | 2479 | 51 |
| H(1B) | -421 | 1108 | 2368 | 51 |
| H(1C) | -375 | 16 | 3054 | 51 |

Table C.6f Torsion angles [deg] for ydp0201.

| | |
|---|---|
| C(12)-N(1)-C(13)-O(2) | -177.38(12) |
| C(15)-N(1)-C(13)-O(2) | 10.92(18) |
| C(12)-N(1)-C(13)-C(9) | 2.36(18) |
| C(15)-N(1)-C(13)-C(9) | -169.35(10) |
| C(6)-C(5)-C(8)-O(1) | -39.77(16) |
| C(4)-C(5)-C(8)-O(1) | 136.85(12) |
| C(6)-C(5)-C(8)-C(9) | 81.62(15) |
| C(4)-C(5)-C(8)-C(9) | -101.76(14) |
| C(16)-C(21)-C(20)-C(19) | -0.2(2) |
| C(16)-C(21)-C(20)-C(22) | -179.47(13) |
| C(6)-C(5)-C(4)-C(3) | 0.49(18) |
| C(8)-C(5)-C(4)-C(3) | -176.27(11) |
| C(20)-C(21)-C(16)-C(17) | 1.5(2) |
| C(20)-C(21)-C(16)-C(15) | -174.66(12) |
| O(2)-C(13)-C(9)-C(10) | -171.34(11) |
| N(1)-C(13)-C(9)-C(10) | 8.92(16) |
| O(2)-C(13)-C(9)-C(14) | 65.58(14) |
| N(1)-C(13)-C(9)-C(14) | -114.16(13) |
| O(2)-C(13)-C(9)-C(8) | -50.71(14) |

| | |
|---|---|
| N(1)-C(13)-C(9)-C(8) | 129.54(11) |
| O(1)-C(8)-C(9)-C(10) | 59.38(13) |
| C(5)-C(8)-C(9)-C(10) | -63.64(14) |
| O(1)-C(8)-C(9)-C(14) | -176.76(10) |
| C(5)-C(8)-C(9)-C(14) | 60.22(14) |
| O(1)-C(8)-C(9)-C(13) | -62.10(12) |
| C(5)-C(8)-C(9)-C(13) | 174.88(10) |
| C(5)-C(4)-C(3)-C(2) | -1.07(19) |
| C(17)-C(18)-C(19)-C(20) | 1.0(2) |
| C(21)-C(20)-C(19)-C(18) | -1.1(2) |
| C(22)-C(20)-C(19)-C(18) | 178.17(13) |
| C(19)-C(18)-C(17)-C(16) | 0.4(2) |
| C(21)-C(16)-C(17)-C(18) | -1.6(2) |
| C(15)-C(16)-C(17)-C(18) | 174.61(12) |
| C(4)-C(3)-C(2)-C(7) | 0.26(19) |
| C(4)-C(3)-C(2)-C(1) | 180.00(12) |
| C(13)-N(1)-C(15)-C(16) | 99.59(14) |
| C(12)-N(1)-C(15)-C(16) | -72.95(14) |
| C(21)-C(16)-C(15)-N(1) | -33.86(18) |
| C(17)-C(16)-C(15)-N(1) | 149.97(12) |
| C(4)-C(5)-C(6)-C(7) | 0.87(19) |
| C(8)-C(5)-C(6)-C(7) | 177.55(12) |
| C(13)-N(1)-C(12)-C(11) | 19.08(19) |
| C(15)-N(1)-C(12)-C(11) | -168.88(12) |
| C(14)-C(9)-C(10)-C(11) | 79.78(14) |
| C(13)-C(9)-C(10)-C(11) | -41.03(15) |
| C(8)-C(9)-C(10)-C(11) | -157.31(11) |
| C(5)-C(6)-C(7)-C(2) | -1.7(2) |
| C(3)-C(2)-C(7)-C(6) | 1.1(2) |
| C(1)-C(2)-C(7)-C(6) | -178.63(13) |
| N(1)-C(12)-C(11)-C(10) | -50.41(17) |
| C(9)-C(10)-C(11)-C(12) | 62.47(16) |

Table C.7f Hydrogen bonds for ydp0201 [A and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(1)-H(1)...O(2)#1 | 0.88(2) | 1.85(2) | 2.7250(13) | 172.5(19) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

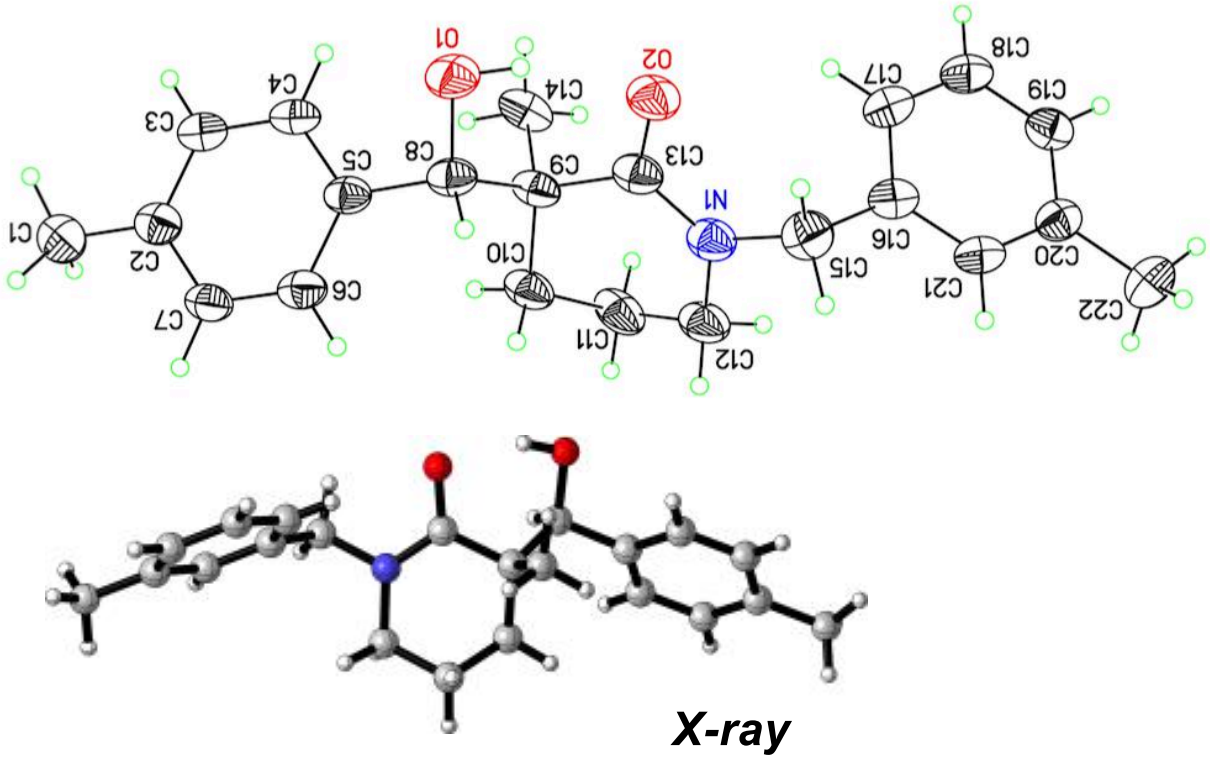



Figure C.7 Structure of ydp0202.

**Structure Determination.**

Colorless needle-like crystals of **ydp0202** were grown from a dichloromethane/hexanes solution of the compound at 22 deg. C. A crystal of dimensions 0.19 x 0.04 x 0.04 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (ë = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ù. The exposure times were 2 sec. for the low angle images, 12 sec. for high angle. The integration of the data yielded a total of 27336 reflections to a maximum 2è value of 136.48° of which 3373 were independent and 2820 were greater than 2ó(I). The final cell constants (Table 1) were based on the xyz centroids 14552 reflections above 10ó(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group P2(1)/c with Z = 4 for the formula $C_{22}H_{27}NO_2$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in both idealized and refined positions. Full matrix least-squares refinement based on $F^2$ converged at R1 = 0.0599 and wR2 = 0.1724 [based on I > 2sigma(I)], R1 = 0.0679 and wR2 = 0.1796 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Table C.1g Crystal data and structure refinement for ydp0202.

| | |
|---|---|
| Identification code | ydp0202 |
| Empirical formula | C22 H27 N O2 |
| Formula weight | 337.44 |
| Temperature | 85(2) K |
| Wavelength | 1.54178 A |
| Crystal system, space group | Monoclinic, P2(1)/c |
| Unit cell dimensions | a = 20.7031(15) A alpha = 90 deg. |
| | b = 6.21010(10) A beta = 105.676(7) deg. |
| | c = 14.8937(3) A gamma = 90 deg. |
| Volume | 1843.63(15) A^3 |
| Z, Calculated density | 4, 1.216 Mg/m^3 |
| Absorption coefficient | 0.602 mm^-1 |
| F(000) | 728 |
| Crystal size | 0.190 x 0.040 x 0.040 mm |
| Theta range for data collection | 4.436 to 68.242 deg. |
| Limiting indices | -24<=h<=24, -7<=k<=7, -16<=l<=17 |
| Reflections collected / unique | 27336 / 3373 [R(int) = 0.0778] |
| Completeness to theta = 67.679 | 99.7 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.000 and 0.773 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 3373 / 0 / 234 |
| Goodness-of-fit on F^2 | 1.094 |
| Final R indices [I>2sigma(I)] | R1 = 0.0599, wR2 = 0.1724 |
| R indices (all data) | R1 = 0.0679, wR2 = 0.1796 |
| Extinction coefficient | 0.0031(8) |
| Largest diff. peak and hole | 0.280 and -0.267 e.A^-3 |

Table C.2g Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for ydp0202. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| N(1) | 8165(1) | 2112(2) | 3557(1) | 40(1) |
| O(1) | 7389(1) | 5155(2) | 5566(1) | 44(1) |
| O(2) | 8117(1) | 5136(2) | 4369(1) | 44(1) |
| C(1) | 4906(1) | 292(3) | 6445(2) | 45(1) |
| C(2) | 5507(1) | 973(3) | 6140(1) | 36(1) |
| C(3) | 5570(1) | 3061(3) | 5836(1) | 38(1) |
| C(4) | 6126(1) | 3684(3) | 5548(1) | 37(1) |
| C(5) | 6646(1) | 2245(3) | 5568(1) | 32(1) |
| C(6) | 6587(1) | 157(3) | 5878(1) | 37(1) |

| | | | | |
|---|---|---|---|---|
| C(7) | 6028(1) | -463(3) | 6154(1) | 37(1) |
| C(8) | 7258(1) | 2968(3) | 5278(1) | 34(1) |
| C(9) | 7189(1) | 2690(3) | 4213(1) | 35(1) |
| C(10) | 7027(1) | 331(3) | 3933(1) | 42(1) |
| C(11) | 7162(1) | -150(3) | 3002(2) | 49(1) |
| C(12) | 7898(1) | 86(3) | 3094(2) | 47(1) |
| C(13) | 7856(1) | 3382(3) | 4046(1) | 37(1) |
| C(14) | 6639(1) | 4186(3) | 3638(2) | 44(1) |
| C(15) | 8849(1) | 2609(3) | 3528(1) | 44(1) |
| C(16) | 8904(1) | 3422(3) | 2596(1) | 36(1) |
| C(17) | 8565(1) | 5286(3) | 2202(2) | 40(1) |
| C(18) | 8664(1) | 6123(3) | 1393(1) | 41(1) |
| C(19) | 9092(1) | 5112(3) | 960(2) | 38(1) |
| C(20) | 9429(1) | 3241(3) | 1328(1) | 36(1) |
| C(21) | 9330(1) | 2428(3) | 2153(1) | 37(1) |
| C(22) | 9906(1) | 2121(4) | 880(2) | 48(1) |

Table C.3g Bond lengths [A] and angles [deg] for ydp0202.

| | |
|---|---|
| N(1)-C(13) | 1.345(3) |
| N(1)-C(15) | 1.461(3) |
| N(1)-C(12) | 1.469(2) |
| O(1)-C(8) | 1.428(2) |
| O(1)-H(1) | 0.88(3) |
| O(2)-C(13) | 1.253(2) |
| C(1)-C(2) | 1.496(3) |
| C(1)-H(1A) | 0.9800 |
| C(1)-H(1B) | 0.9800 |
| C(1)-H(1C) | 0.9800 |
| C(2)-C(3) | 1.391(3) |
| C(2)-C(7) | 1.395(3) |
| C(3)-C(4) | 1.388(3) |
| C(3)-H(3) | 0.9500 |
| C(4)-C(5) | 1.392(2) |
| C(4)-H(4) | 0.9500 |
| C(5)-C(6) | 1.393(2) |
| C(5)-C(8) | 1.514(3) |
| C(6)-C(7) | 1.383(3) |
| C(6)-H(6) | 0.9500 |
| C(7)-H(7) | 0.9500 |
| C(8)-C(9) | 1.562(3) |
| C(8)-H(8) | 1.0000 |
| C(9)-C(13) | 1.530(3) |
| C(9)-C(10) | 1.535(2) |

| | |
|---|---|
| C(9)-C(14) | 1.539(2) |
| C(10)-C(11) | 1.516(3) |
| C(10)-H(10A) | 0.9900 |
| C(10)-H(10B) | 0.9900 |
| C(11)-C(12) | 1.500(3) |
| C(11)-H(11A) | 0.9900 |
| C(11)-H(11B) | 0.9900 |
| C(12)-H(12A) | 0.9900 |
| C(12)-H(12B) | 0.9900 |
| C(14)-H(14A) | 0.9800 |
| C(14)-H(14B) | 0.9800 |
| C(14)-H(14C) | 0.9800 |
| C(15)-C(16) | 1.510(3) |
| C(15)-H(15A) | 0.9900 |
| C(15)-H(15B) | 0.9900 |
| C(16)-C(21) | 1.382(3) |
| C(16)-C(17) | 1.397(2) |
| C(17)-C(18) | 1.378(3) |
| C(17)-H(17) | 0.9500 |
| C(18)-C(19) | 1.380(3) |
| C(18)-H(18) | 0.9500 |
| C(19)-C(20) | 1.389(2) |
| C(19)-H(19) | 0.9500 |
| C(20)-C(21) | 1.394(3) |
| C(20)-C(22) | 1.502(3) |
| C(21)-H(21) | 0.9500 |
| C(22)-H(22A) | 0.9800 |
| C(22)-H(22B) | 0.9800 |
| C(22)-H(22C) | 0.9800 |
| C(13)-N(1)-C(15) | 119.80(16) |
| C(13)-N(1)-C(12) | 125.71(17) |
| C(15)-N(1)-C(12) | 114.27(17) |
| C(8)-O(1)-H(1) | 100(2) |
| C(2)-C(1)-H(1A) | 109.5 |
| C(2)-C(1)-H(1B) | 109.5 |
| H(1A)-C(1)-H(1B) | 109.5 |
| C(2)-C(1)-H(1C) | 109.5 |
| H(1A)-C(1)-H(1C) | 109.5 |
| H(1B)-C(1)-H(1C) | 109.5 |
| C(3)-C(2)-C(7) | 117.45(17) |
| C(3)-C(2)-C(1) | 121.41(17) |
| C(7)-C(2)-C(1) | 121.15(17) |
| C(4)-C(3)-C(2) | 121.24(17) |
| C(4)-C(3)-H(3) | 119.4 |
| C(2)-C(3)-H(3) | 119.4 |
| C(3)-C(4)-C(5) | 121.03(17) |

| | |
|---|---|
| C(3)-C(4)-H(4) | 119.5 |
| C(5)-C(4)-H(4) | 119.5 |
| C(4)-C(5)-C(6) | 117.91(17) |
| C(4)-C(5)-C(8) | 120.35(16) |
| C(6)-C(5)-C(8) | 121.73(16) |
| C(7)-C(6)-C(5) | 120.84(17) |
| C(7)-C(6)-H(6) | 119.6 |
| C(5)-C(6)-H(6) | 119.6 |
| C(6)-C(7)-C(2) | 121.51(17) |
| C(6)-C(7)-H(7) | 119.2 |
| C(2)-C(7)-H(7) | 119.2 |
| O(1)-C(8)-C(5) | 107.54(15) |
| O(1)-C(8)-C(9) | 111.61(15) |
| C(5)-C(8)-C(9) | 113.77(14) |
| O(1)-C(8)-H(8) | 107.9 |
| C(5)-C(8)-H(8) | 107.9 |
| C(9)-C(8)-H(8) | 107.9 |
| C(13)-C(9)-C(10) | 111.35(16) |
| C(13)-C(9)-C(14) | 107.73(15) |
| C(10)-C(9)-C(14) | 110.52(15) |
| C(13)-C(9)-C(8) | 107.17(14) |
| C(10)-C(9)-C(8) | 109.56(15) |
| C(14)-C(9)-C(8) | 110.45(16) |
| C(11)-C(10)-C(9) | 110.84(16) |
| C(11)-C(10)-H(10A) | 109.5 |
| C(9)-C(10)-H(10A) | 109.5 |
| C(11)-C(10)-H(10B) | 109.5 |
| C(9)-C(10)-H(10B) | 109.5 |
| H(10A)-C(10)-H(10B) | 108.1 |
| C(12)-C(11)-C(10) | 109.35(18) |
| C(12)-C(11)-H(11A) | 109.8 |
| C(10)-C(11)-H(11A) | 109.8 |
| C(12)-C(11)-H(11B) | 109.8 |
| C(10)-C(11)-H(11B) | 109.8 |
| H(11A)-C(11)-H(11B) | 108.3 |
| N(1)-C(12)-C(11) | 111.69(17) |
| N(1)-C(12)-H(12A) | 109.3 |
| C(11)-C(12)-H(12A) | 109.3 |
| N(1)-C(12)-H(12B) | 109.3 |
| C(11)-C(12)-H(12B) | 109.3 |
| H(12A)-C(12)-H(12B) | 107.9 |
| O(2)-C(13)-N(1) | 119.99(18) |
| O(2)-C(13)-C(9) | 119.71(17) |
| N(1)-C(13)-C(9) | 120.30(15) |
| C(9)-C(14)-H(14A) | 109.5 |
| C(9)-C(14)-H(14B) | 109.5 |

| | |
|---|---|
| H(14A)-C(14)-H(14B) | 109.5 |
| C(9)-C(14)-H(14C) | 109.5 |
| H(14A)-C(14)-H(14C) | 109.5 |
| H(14B)-C(14)-H(14C) | 109.5 |
| N(1)-C(15)-C(16) | 114.33(16) |
| N(1)-C(15)-H(15A) | 108.7 |
| C(16)-C(15)-H(15A) | 108.7 |
| N(1)-C(15)-H(15B) | 108.7 |
| C(16)-C(15)-H(15B) | 108.7 |
| H(15A)-C(15)-H(15B) | 107.6 |
| C(21)-C(16)-C(17) | 118.80(18) |
| C(21)-C(16)-C(15) | 120.43(16) |
| C(17)-C(16)-C(15) | 120.59(18) |
| C(18)-C(17)-C(16) | 120.23(19) |
| C(18)-C(17)-H(17) | 119.9 |
| C(16)-C(17)-H(17) | 119.9 |
| C(17)-C(18)-C(19) | 120.17(17) |
| C(17)-C(18)-H(18) | 119.9 |
| C(19)-C(18)-H(18) | 119.9 |
| C(18)-C(19)-C(20) | 120.95(19) |
| C(18)-C(19)-H(19) | 119.5 |
| C(20)-C(19)-H(19) | 119.5 |
| C(19)-C(20)-C(21) | 118.18(18) |
| C(19)-C(20)-C(22) | 122.17(19) |
| C(21)-C(20)-C(22) | 119.64(17) |
| C(16)-C(21)-C(20) | 121.65(16) |
| C(16)-C(21)-H(21) | 119.2 |
| C(20)-C(21)-H(21) | 119.2 |
| C(20)-C(22)-H(22A) | 109.5 |
| C(20)-C(22)-H(22B) | 109.5 |
| H(22A)-C(22)-H(22B) | 109.5 |
| C(20)-C(22)-H(22C) | 109.5 |
| H(22A)-C(22)-H(22C) | 109.5 |
| H(22B)-C(22)-H(22C) | 109.5 |

Table C.4g Anisotropic displacement parameters (A^2 x 10^3) for ydp0202. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| N(1) | 51(1) | 32(1) | 35(1) | -2(1) | 10(1) | -4(1) |
| O(1) | 48(1) | 32(1) | 49(1) | -15(1) | 11(1) | -10(1) |
| O(2) | 50(1) | 33(1) | 48(1) | -9(1) | 11(1) | -11(1) |
| C(1) | 50(1) | 44(1) | 40(1) | -2(1) | 8(1) | -6(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(2) | 42(1) | 33(1) | 31(1) | -4(1) | 3(1) | -3(1) |
| C(3) | 40(1) | 29(1) | 41(1) | -2(1) | 6(1) | 3(1) |
| C(4) | 44(1) | 23(1) | 40(1) | -1(1) | 5(1) | 3(1) |
| C(5) | 41(1) | 25(1) | 28(1) | -4(1) | 3(1) | 0(1) |
| C(6) | 47(1) | 29(1) | 31(1) | 0(1) | 5(1) | 6(1) |
| C(7) | 53(1) | 26(1) | 31(1) | 1(1) | 8(1) | 0(1) |
| C(8) | 42(1) | 26(1) | 33(1) | -4(1) | 4(1) | 1(1) |
| C(9) | 45(1) | 24(1) | 32(1) | 1(1) | 5(1) | -4(1) |
| C(10) | 63(1) | 27(1) | 34(1) | -2(1) | 12(1) | -9(1) |
| C(11) | 78(2) | 34(1) | 36(1) | -9(1) | 18(1) | -23(1) |
| C(12) | 76(1) | 28(1) | 40(1) | -6(1) | 21(1) | -7(1) |
| C(13) | 46(1) | 29(1) | 33(1) | -1(1) | 5(1) | -3(1) |
| C(14) | 46(1) | 34(1) | 45(1) | 10(1) | 0(1) | -7(1) |
| C(15) | 48(1) | 45(1) | 38(1) | 2(1) | 8(1) | 4(1) |
| C(16) | 38(1) | 30(1) | 37(1) | -2(1) | 3(1) | 3(1) |
| C(17) | 42(1) | 35(1) | 42(1) | -4(1) | 7(1) | 7(1) |
| C(18) | 43(1) | 32(1) | 43(1) | 1(1) | 2(1) | 7(1) |
| C(19) | 37(1) | 35(1) | 38(1) | 4(1) | 2(1) | -1(1) |
| C(20) | 34(1) | 34(1) | 39(1) | -6(1) | 5(1) | 0(1) |
| C(21) | 39(1) | 28(1) | 39(1) | -1(1) | 3(1) | 6(1) |
| C(22) | 42(1) | 56(1) | 46(1) | -4(1) | 9(1) | 10(1) |

Table C.5g Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for ydp0202.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 7675(15) | 5510(50) | 5250(20) | 72(9) |
| H(1A) | 4657 | 1570 | 6546 | 68 |
| H(1B) | 5051 | -527 | 7027 | 68 |
| H(1C) | 4616 | -612 | 5962 | 68 |
| H(3) | 5226 | 4080 | 5825 | 46 |
| H(4) | 6153 | 5114 | 5335 | 44 |
| H(6) | 6935 | -855 | 5901 | 44 |
| H(7) | 5998 | -1900 | 6358 | 45 |
| H(8) | 7648 | 2080 | 5627 | 41 |
| H(10A) | 7305 | -625 | 4417 | 50 |
| H(10B) | 6550 | 39 | 3891 | 50 |
| H(11A) | 7017 | -1635 | 2804 | 59 |
| H(11B) | 6905 | 858 | 2523 | 59 |
| H(12A) | 8142 | -1140 | 3458 | 56 |
| H(12B) | 7976 | 43 | 2467 | 56 |
| H(14A) | 6638 | 4121 | 2980 | 66 |

| | | | | |
|---|---|---|---|---|
| H(14B) | 6728 | 5668 | 3865 | 66 |
| H(14C) | 6201 | 3724 | 3702 | 66 |
| H(15A) | 9126 | 1294 | 3693 | 53 |
| H(15B) | 9037 | 3710 | 4009 | 53 |
| H(17) | 8266 | 5978 | 2494 | 48 |
| H(18) | 8436 | 7400 | 1132 | 49 |
| H(19) | 9158 | 5704 | 403 | 46 |
| H(21) | 9560 | 1158 | 2416 | 44 |
| H(22A) | 9933 | 2924 | 325 | 72 |
| H(22B) | 9744 | 659 | 700 | 72 |
| H(22C) | 10352 | 2050 | 1324 | 72 |

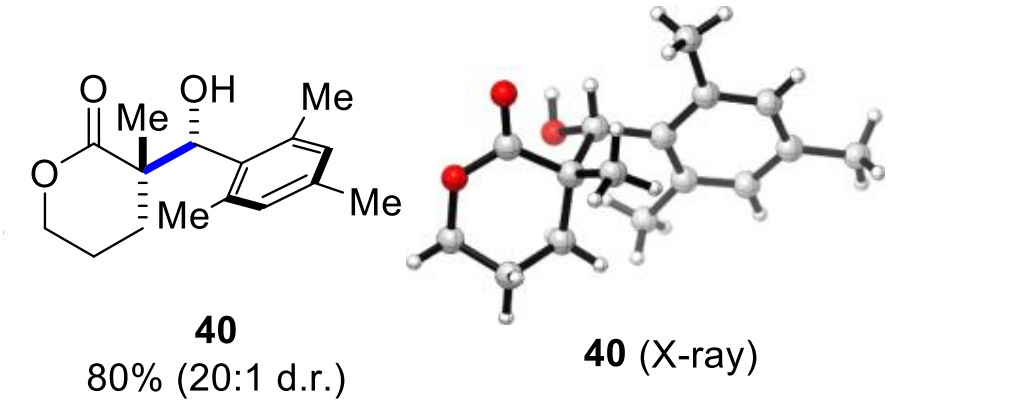
Table C.6g Torsion angles [deg] for ydp0202.

| | |
|---|---|
| C(7)-C(2)-C(3)-C(4) | 0.7(3) |
| C(1)-C(2)-C(3)-C(4) | -179.62(17) |
| C(2)-C(3)-C(4)-C(5) | -1.0(3) |
| C(3)-C(4)-C(5)-C(6) | 0.5(3) |
| C(3)-C(4)-C(5)-C(8) | -178.29(17) |
| C(4)-C(5)-C(6)-C(7) | 0.2(3) |
| C(8)-C(5)-C(6)-C(7) | 179.01(16) |
| C(5)-C(6)-C(7)-C(2) | -0.5(3) |
| C(3)-C(2)-C(7)-C(6) | 0.1(3) |
| C(1)-C(2)-C(7)-C(6) | -179.64(17) |
| C(4)-C(5)-C(8)-O(1) | 35.1(2) |
| C(6)-C(5)-C(8)-O(1) | -143.70(17) |
| C(4)-C(5)-C(8)-C(9) | -89.09(19) |
| C(6)-C(5)-C(8)-C(9) | 92.2(2) |
| O(1)-C(8)-C(9)-C(13) | 60.85(18) |
| C(5)-C(8)-C(9)-C(13) | -177.23(13) |
| O(1)-C(8)-C(9)-C(10) | -178.22(15) |
| C(5)-C(8)-C(9)-C(10) | -56.30(19) |
| O(1)-C(8)-C(9)-C(14) | -56.25(19) |
| C(5)-C(8)-C(9)-C(14) | 65.67(18) |
| C(13)-C(9)-C(10)-C(11) | -44.5(2) |
| C(14)-C(9)-C(10)-C(11) | 75.2(2) |
| C(8)-C(9)-C(10)-C(11) | -162.85(17) |
| C(9)-C(10)-C(11)-C(12) | 64.6(2) |
| C(13)-N(1)-C(12)-C(11) | 15.3(3) |
| C(15)-N(1)-C(12)-C(11) | -170.24(17) |
| C(10)-C(11)-C(12)-N(1) | -48.4(2) |
| C(15)-N(1)-C(13)-O(2) | 9.6(3) |
| C(12)-N(1)-C(13)-O(2) | -176.21(18) |
| C(15)-N(1)-C(13)-C(9) | -170.11(16) |

| | |
|---|---|
| C(12)-N(1)-C(13)-C(9) | 4.1(3) |
| C(10)-C(9)-C(13)-O(2) | -168.80(16) |
| C(14)-C(9)-C(13)-O(2) | 69.9(2) |
| C(8)-C(9)-C(13)-O(2) | -49.0(2) |
| C(10)-C(9)-C(13)-N(1) | 10.9(2) |
| C(14)-C(9)-C(13)-N(1) | -110.42(19) |
| C(8)-C(9)-C(13)-N(1) | 130.71(17) |
| C(13)-N(1)-C(15)-C(16) | -109.3(2) |
| C(12)-N(1)-C(15)-C(16) | 75.9(2) |
| N(1)-C(15)-C(16)-C(21) | -125.77(18) |
| N(1)-C(15)-C(16)-C(17) | 59.1(2) |
| C(21)-C(16)-C(17)-C(18) | -0.9(3) |
| C(15)-C(16)-C(17)-C(18) | 174.32(18) |
| C(16)-C(17)-C(18)-C(19) | 0.7(3) |
| C(17)-C(18)-C(19)-C(20) | 0.2(3) |
| C(18)-C(19)-C(20)-C(21) | -0.8(3) |
| C(18)-C(19)-C(20)-C(22) | -179.16(17) |
| C(17)-C(16)-C(21)-C(20) | 0.2(3) |
| C(15)-C(16)-C(21)-C(20) | -175.02(17) |
| C(19)-C(20)-C(21)-C(16) | 0.7(3) |
| C(22)-C(20)-C(21)-C(16) | 179.03(17) |

Table C.7g Hydrogen bonds for ydp0202 [A and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(1)-H(1)...O(2) | 0.88(3) | 1.80(3) | 2.627(2) | 155(3) |



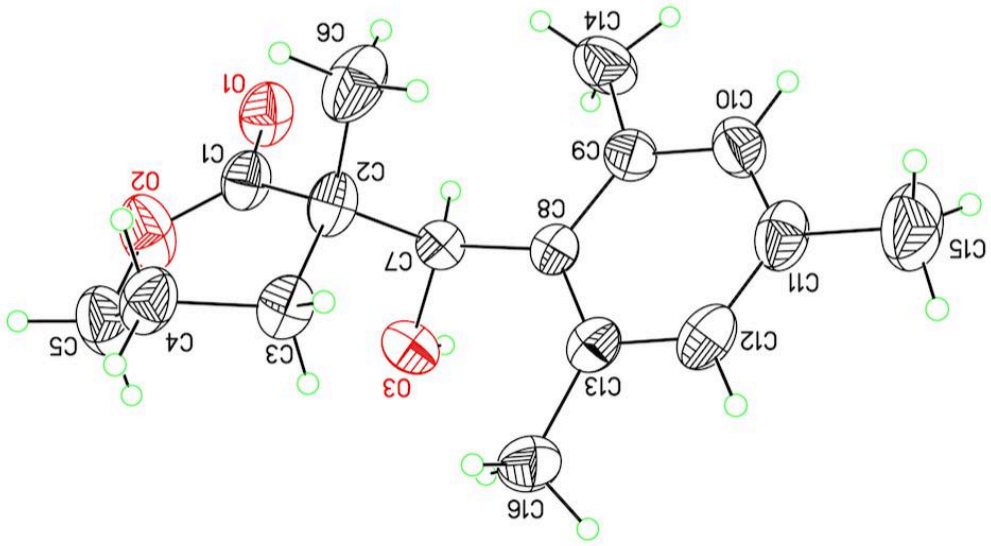




Figure C.8 Structure of yd6mes.

**Structure Determination.**

Colorless block-like crystals of **yd6mes** were grown from a dichloromethane/hexane solution of the compound at 22 deg. C. A crystal of dimensions 0.16 x 0.10 x 0.10 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (ë = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 225(1) K with the detector placed at a distance 42.00 mm from the crystal. The crystals undergo a destructive phase change that prevented examination at lower temperature. A total of 2028 images were collected with an oscillation width of 1.0° in ù. The exposure times were 1 sec. for the low angle images, 8 sec. for high angle. The integration of the data yielded a total of 21906 reflections to a maximum 2è value of 136.44° of which 2649 were independent and 2480 were greater than 2ó(I). The final cell constants (Table 1) were based on the xyz centroids 14378 reflections above 10ó(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the

space group P2(1)/n with Z = 4 for the formula $C_{16}H_{22}O_3$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in a combination of idealized and refined positions. Full matrix least-squares refinement based on $F^2$ converged at R1 = 0.0466 and wR2 = 0.1269 [based on I > 2sigma(I)], R1 = 0.0481 and wR2 = 0.1284 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.
Sheldrick, G.M. SHELXTL, v. 2014/6; Bruker Analytical X-ray, Madison, WI, 2014.
CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

Table C.1h Crystal data and structure refinement for yd6mes.

| | |
|---|---|
| Identification code | yd6mes |
| Empirical formula | C16 H22 O3 |
| Formula weight | 262.33 |
| Temperature | 225(2) K |
| Wavelength | 1.54178 A |
| Crystal system, space group | Monoclinic, P2(1)/n |
| Unit cell dimensions | a = 14.4244(3) A alpha = 90 deg. |
| | b = 8.04450(10) A beta = 119.580(8) deg. |
| | c = 14.4441(10) A gamma = 90 deg. |
| Volume | 1457.61(15) A^3 |
| Z, Calculated density | 4, 1.195 Mg/m^3 |
| Absorption coefficient | 0.649 mm^-1 |
| F(000) | 568 |
| Crystal size | 0.160 x 0.100 x 0.100 mm |
| Theta range for data collection | 3.543 to 68.219 deg. |
| Limiting indices | -17<=h<=17, -8<=k<=9, -17<=l<=17 |
| Reflections collected / unique | 21906 / 2649 [R(int) = 0.0420] |
| Completeness to theta = 67.679 | 99.7 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.937 and 0.781 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 2649 / 3 / 205 |
| Goodness-of-fit on F^2 | 1.054 |
| Final R indices [I>2sigma(I)] | R1 = 0.0466, wR2 = 0.1269 |
| R indices (all data) | R1 = 0.0481, wR2 = 0.1284 |
| Extinction coefficient | 0.0154(13) |
| Largest diff. peak and hole | 0.230 and -0.249 e.A^-3 |

Table C.2h Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for yd6mes. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| x | y | z | U(eq) |
|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| O(1) | 3289(1) | 3778(1) | 8312(1) | 51(1) |
| O(2) | 2771(1) | 2258(2) | 6910(1) | 63(1) |
| O(3) | 2913(1) | 6343(1) | 6300(1) | 41(1) |
| C(1) | 3397(1) | 3440(2) | 7553(1) | 41(1) |
| C(2) | 4235(1) | 4322(2) | 7365(1) | 41(1) |
| C(3) | 4180(3) | 3677(5) | 6302(3) | 42(1) |
| C(4) | 3891(2) | 1864(3) | 6133(2) | 51(1) |
| C(5) | 2784(5) | 1701(8) | 5968(6) | 60(2) |
| C(3A) | 4535(7) | 3506(13) | 6678(8) | 44(2) |
| C(4A) | 3544(5) | 2763(9) | 5779(5) | 53(2) |
| C(5A) | 3105(12) | 1465(19) | 6177(15) | 62(4) |
| C(6) | 5307(1) | 4017(2) | 8373(2) | 63(1) |
| C(6A) | 5307(1) | 4017(2) | 8373(2) | 63(1) |
| C(7) | 3916(1) | 6195(2) | 7253(1) | 32(1) |
| C(8) | 4762(1) | 7401(2) | 7319(1) | 32(1) |
| C(9) | 5406(1) | 8196(2) | 8307(1) | 38(1) |
| C(10) | 6244(1) | 9214(2) | 8442(1) | 46(1) |
| C(11) | 6458(1) | 9527(2) | 7627(1) | 48(1) |
| C(12) | 5782(1) | 8830(2) | 6647(1) | 45(1) |
| C(13) | 4934(1) | 7795(2) | 6464(1) | 37(1) |
| C(14) | 5206(1) | 8065(3) | 9240(1) | 59(1) |
| C(15) | 7376(1) | 10627(3) | 7793(2) | 75(1) |
| C(16) | 4233(1) | 7245(2) | 5325(1) | 54(1) |

Table C.3h Bond lengths [A] and angles [deg] for yd6mes.

| | |
|---|---|
| O(1)-C(1) | 1.2126(17) |
| O(2)-C(1) | 1.3246(18) |
| O(2)-C(5) | 1.441(8) |
| O(2)-C(5A) | 1.505(19) |
| O(3)-C(7) | 1.4263(15) |
| O(3)-H(3) | 0.91(2) |
| C(1)-C(2) | 1.5356(18) |
| C(2)-C(3A) | 1.424(11) |
| C(2)-C(6A) | 1.533(2) |
| C(2)-C(6) | 1.533(2) |
| C(2)-C(7) | 1.5602(18) |
| C(2)-C(3) | 1.586(4) |
| C(3)-C(4) | 1.503(5) |
| C(3)-H(3A) | 0.9800 |
| C(3)-H(3B) | 0.9800 |
| C(4)-C(5) | 1.499(6) |

| | |
|---|---|
| C(4)-H(4A) | 0.9800 |
| C(4)-H(4B) | 0.9800 |
| C(5)-H(5A) | 0.9800 |
| C(5)-H(5B) | 0.9800 |
| C(3A)-C(4A) | 1.502(9) |
| C(3A)-H(3C) | 0.9800 |
| C(3A)-H(3D) | 0.9800 |
| C(4A)-C(5A) | 1.477(14) |
| C(4A)-H(4C) | 0.9800 |
| C(4A)-H(4D) | 0.9800 |
| C(5A)-H(5C) | 0.9800 |
| C(5A)-H(5D) | 0.9800 |
| C(6)-H(6A) | 0.9700 |
| C(6)-H(6B) | 0.9700 |
| C(6)-H(6C) | 0.9700 |
| C(6A)-H(6D) | 0.9700 |
| C(6A)-H(6E) | 0.9700 |
| C(6A)-H(6F) | 0.9700 |
| C(7)-C(8) | 1.5248(17) |
| C(7)-H(7) | 0.9900 |
| C(8)-C(13) | 1.4097(17) |
| C(8)-C(9) | 1.4146(18) |
| C(9)-C(10) | 1.3911(19) |
| C(9)-C(14) | 1.515(2) |
| C(10)-C(11) | 1.380(2) |
| C(10)-H(10) | 0.9400 |
| C(11)-C(12) | 1.381(2) |
| C(11)-C(15) | 1.510(2) |
| C(12)-C(13) | 1.393(2) |
| C(12)-H(12) | 0.9400 |
| C(13)-C(16) | 1.511(2) |
| C(14)-H(14A) | 0.9700 |
| C(14)-H(14B) | 0.9700 |
| C(14)-H(14C) | 0.9700 |
| C(15)-H(15A) | 0.9700 |
| C(15)-H(15B) | 0.9700 |
| C(15)-H(15C) | 0.9700 |
| C(16)-H(16A) | 0.9700 |
| C(16)-H(16B) | 0.9700 |
| C(16)-H(16C) | 0.9700 |
| C(1)-O(2)-C(5) | 124.3(2) |
| C(1)-O(2)-C(5A) | 116.9(6) |
| C(7)-O(3)-H(3) | 105.6(13) |
| O(1)-C(1)-O(2) | 116.58(12) |
| O(1)-C(1)-C(2) | 121.27(13) |
| O(2)-C(1)-C(2) | 122.14(12) |

| | |
|---|---|
| C(3A)-C(2)-C(6A) | 94.4(4) |
| C(3A)-C(2)-C(1) | 116.5(4) |
| C(6A)-C(2)-C(1) | 105.73(12) |
| C(6)-C(2)-C(1) | 105.73(12) |
| C(3A)-C(2)-C(7) | 123.2(4) |
| C(6A)-C(2)-C(7) | 111.17(12) |
| C(6)-C(2)-C(7) | 111.17(12) |
| C(1)-C(2)-C(7) | 104.35(10) |
| C(6)-C(2)-C(3) | 114.35(18) |
| C(1)-C(2)-C(3) | 110.60(18) |
| C(7)-C(2)-C(3) | 110.11(16) |
| C(4)-C(3)-C(2) | 110.6(3) |
| C(4)-C(3)-H(3A) | 109.5 |
| C(2)-C(3)-H(3A) | 109.5 |
| C(4)-C(3)-H(3B) | 109.5 |
| C(2)-C(3)-H(3B) | 109.5 |
| H(3A)-C(3)-H(3B) | 108.1 |
| C(5)-C(4)-C(3) | 107.4(4) |
| C(5)-C(4)-H(4A) | 110.2 |
| C(3)-C(4)-H(4A) | 110.2 |
| C(5)-C(4)-H(4B) | 110.2 |
| C(3)-C(4)-H(4B) | 110.2 |
| H(4A)-C(4)-H(4B) | 108.5 |
| O(2)-C(5)-C(4) | 109.3(5) |
| O(2)-C(5)-H(5A) | 109.8 |
| C(4)-C(5)-H(5A) | 109.8 |
| O(2)-C(5)-H(5B) | 109.8 |
| C(4)-C(5)-H(5B) | 109.8 |
| H(5A)-C(5)-H(5B) | 108.3 |
| C(2)-C(3A)-C(4A) | 107.4(7) |
| C(2)-C(3A)-H(3C) | 110.2 |
| C(4A)-C(3A)-H(3C) | 110.2 |
| C(2)-C(3A)-H(3D) | 110.2 |
| C(4A)-C(3A)-H(3D) | 110.2 |
| H(3C)-C(3A)-H(3D) | 108.5 |
| C(5A)-C(4A)-C(3A) | 110.6(10) |
| C(5A)-C(4A)-H(4C) | 109.5 |
| C(3A)-C(4A)-H(4C) | 109.5 |
| C(5A)-C(4A)-H(4D) | 109.5 |
| C(3A)-C(4A)-H(4D) | 109.5 |
| H(4C)-C(4A)-H(4D) | 108.1 |
| C(4A)-C(5A)-O(2) | 108.8(11) |
| C(4A)-C(5A)-H(5C) | 109.9 |
| O(2)-C(5A)-H(5C) | 109.9 |
| C(4A)-C(5A)-H(5D) | 109.9 |
| O(2)-C(5A)-H(5D) | 109.9 |

| | |
|---|---|
| H(5C)-C(5A)-H(5D) | 108.3 |
| C(2)-C(6)-H(6A) | 109.5 |
| C(2)-C(6)-H(6B) | 109.5 |
| H(6A)-C(6)-H(6B) | 109.5 |
| C(2)-C(6)-H(6C) | 109.5 |
| H(6A)-C(6)-H(6C) | 109.5 |
| H(6B)-C(6)-H(6C) | 109.5 |
| C(2)-C(6A)-H(6D) | 109.5 |
| C(2)-C(6A)-H(6E) | 109.5 |
| H(6D)-C(6A)-H(6E) | 109.5 |
| C(2)-C(6A)-H(6F) | 109.5 |
| H(6D)-C(6A)-H(6F) | 109.5 |
| H(6E)-C(6A)-H(6F) | 109.5 |
| O(3)-C(7)-C(8) | 113.99(10) |
| O(3)-C(7)-C(2) | 106.71(10) |
| C(8)-C(7)-C(2) | 114.96(10) |
| O(3)-C(7)-H(7) | 106.9 |
| C(8)-C(7)-H(7) | 106.9 |
| C(2)-C(7)-H(7) | 106.9 |
| C(13)-C(8)-C(9) | 118.05(11) |
| C(13)-C(8)-C(7) | 124.72(11) |
| C(9)-C(8)-C(7) | 117.22(11) |
| C(10)-C(9)-C(8) | 119.98(12) |
| C(10)-C(9)-C(14) | 116.78(13) |
| C(8)-C(9)-C(14) | 123.18(12) |
| C(11)-C(10)-C(9) | 122.21(13) |
| C(11)-C(10)-H(10) | 118.9 |
| C(9)-C(10)-H(10) | 118.9 |
| C(10)-C(11)-C(12) | 117.26(12) |
| C(10)-C(11)-C(15) | 121.30(16) |
| C(12)-C(11)-C(15) | 121.42(15) |
| C(11)-C(12)-C(13) | 123.13(13) |
| C(11)-C(12)-H(12) | 118.4 |
| C(13)-C(12)-H(12) | 118.4 |
| C(12)-C(13)-C(8) | 119.09(12) |
| C(12)-C(13)-C(16) | 115.71(12) |
| C(8)-C(13)-C(16) | 125.14(12) |
| C(9)-C(14)-H(14A) | 109.5 |
| C(9)-C(14)-H(14B) | 109.5 |
| H(14A)-C(14)-H(14B) | 109.5 |
| C(9)-C(14)-H(14C) | 109.5 |
| H(14A)-C(14)-H(14C) | 109.5 |
| H(14B)-C(14)-H(14C) | 109.5 |
| C(11)-C(15)-H(15A) | 109.5 |
| C(11)-C(15)-H(15B) | 109.5 |
| H(15A)-C(15)-H(15B) | 109.5 |

| | |
|---|---|
| C(11)-C(15)-H(15C) | 109.5 |
| H(15A)-C(15)-H(15C) | 109.5 |
| H(15B)-C(15)-H(15C) | 109.5 |
| C(13)-C(16)-H(16A) | 109.5 |
| C(13)-C(16)-H(16B) | 109.5 |
| H(16A)-C(16)-H(16B) | 109.5 |
| C(13)-C(16)-H(16C) | 109.5 |
| H(16A)-C(16)-H(16C) | 109.5 |
| H(16B)-C(16)-H(16C) | 109.5 |

Table C.4h Anisotropic displacement parameters (A^2 x 10^3) for yd6mes. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| O(1) | 64(1) | 48(1) | 60(1) | -2(1) | 45(1) | -8(1) |
| O(2) | 74(1) | 65(1) | 74(1) | -23(1) | 54(1) | -32(1) |
| O(3) | 30(1) | 51(1) | 41(1) | -7(1) | 16(1) | 3(1) |
| C(1) | 45(1) | 37(1) | 53(1) | 1(1) | 32(1) | -2(1) |
| C(2) | 41(1) | 34(1) | 60(1) | 2(1) | 34(1) | 0(1) |
| C(3) | 48(2) | 39(1) | 53(2) | 1(1) | 36(2) | 3(1) |
| C(4) | 73(2) | 36(1) | 58(1) | 1(1) | 44(1) | 6(1) |
| C(5) | 75(3) | 56(3) | 61(2) | -15(2) | 44(3) | -24(3) |
| C(3A) | 46(5) | 39(4) | 56(6) | 2(4) | 34(4) | 2(3) |
| C(5A) | 75(8) | 47(5) | 81(10) | -23(5) | 51(8) | 1(5) |
| C(6) | 42(1) | 50(1) | 96(1) | 24(1) | 32(1) | 11(1) |
| C(6A) | 42(1) | 50(1) | 96(1) | 24(1) | 32(1) | 11(1) |
| C(7) | 30(1) | 36(1) | 35(1) | -1(1) | 18(1) | 1(1) |
| C(8) | 32(1) | 30(1) | 37(1) | 2(1) | 19(1) | 3(1) |
| C(9) | 36(1) | 39(1) | 38(1) | 0(1) | 18(1) | 1(1) |
| C(10) | 38(1) | 41(1) | 50(1) | -3(1) | 16(1) | -4(1) |
| C(11) | 37(1) | 40(1) | 67(1) | 8(1) | 26(1) | 0(1) |
| C(12) | 49(1) | 41(1) | 58(1) | 10(1) | 37(1) | 5(1) |
| C(13) | 42(1) | 33(1) | 41(1) | 4(1) | 26(1) | 5(1) |
| C(14) | 62(1) | 75(1) | 40(1) | -13(1) | 27(1) | -16(1) |
| C(15) | 53(1) | 71(1) | 99(1) | 12(1) | 37(1) | -17(1) |
| C(16) | 76(1) | 54(1) | 41(1) | 0(1) | 35(1) | -6(1) |

Table C.5h Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for yd6mes.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(3) | 2554(17) | 7150(30) | 6433(17) | 70(6) |
| H(3A) | 3646 | 4320 | 5696 | 50 |
| H(3B) | 4872 | 3843 | 6343 | 50 |
| H(4A) | 3918 | 1449 | 5509 | 61 |
| H(4B) | 4393 | 1218 | 6756 | 61 |
| H(5A) | 2289 | 2372 | 5355 | 71 |
| H(5B) | 2553 | 538 | 5822 | 71 |
| H(3C) | 5059 | 2633 | 7067 | 52 |
| H(3D) | 4854 | 4303 | 6403 | 52 |
| H(4C) | 3011 | 3636 | 5422 | 63 |
| H(4D) | 3712 | 2277 | 5256 | 63 |
| H(5C) | 3646 | 612 | 6561 | 75 |
| H(5D) | 2490 | 933 | 5578 | 75 |
| H(6A) | 5276 | 4434 | 8988 | 95 |
| H(6B) | 5867 | 4589 | 8313 | 95 |
| H(6C) | 5456 | 2834 | 8457 | 95 |
| H(6D) | 5521 | 2870 | 8386 | 95 |
| H(6E) | 5237 | 4237 | 8996 | 95 |
| H(6F) | 5842 | 4751 | 8375 | 95 |
| H(7) | 3792 | 6464 | 7852 | 39 |
| H(10) | 6678 | 9704 | 9110 | 55 |
| H(12) | 5900 | 9064 | 6075 | 54 |
| H(14A) | 5686 | 8805 | 9804 | 88 |
| H(14B) | 5328 | 6930 | 9501 | 88 |
| H(14C) | 4474 | 8376 | 9012 | 88 |
| H(15A) | 7313 | 10892 | 7109 | 112 |
| H(15B) | 8043 | 10051 | 8232 | 112 |
| H(15C) | 7360 | 11646 | 8144 | 112 |
| H(16A) | 4243 | 8084 | 4848 | 81 |
| H(16B) | 3509 | 7094 | 5187 | 81 |
| H(16C) | 4498 | 6203 | 5208 | 81 |

Table C.6h Torsion angles [deg] for yd6mes.

| | |
|---|---|
| C(5)-O(2)-C(1)-O(1) | 179.6(3) |
| C(5A)-O(2)-C(1)-O(1) | -161.9(7) |
| C(5)-O(2)-C(1)-C(2) | -1.5(4) |
| C(5A)-O(2)-C(1)-C(2) | 17.0(7) |
| O(1)-C(1)-C(2)-C(3A) | 160.6(4) |
| O(2)-C(1)-C(2)-C(3A) | -18.3(5) |
| O(1)-C(1)-C(2)-C(6A) | 57.33(18) |

| | |
|---|---|
| O(2)-C(1)-C(2)-C(6A) | -121.49(16) |
| O(1)-C(1)-C(2)-C(6) | 57.33(18) |
| O(2)-C(1)-C(2)-C(6) | -121.49(16) |
| O(1)-C(1)-C(2)-C(7) | -60.01(17) |
| O(2)-C(1)-C(2)-C(7) | 121.17(15) |
| O(1)-C(1)-C(2)-C(3) | -178.38(18) |
| O(2)-C(1)-C(2)-C(3) | 2.8(2) |
| C(6)-C(2)-C(3)-C(4) | 84.8(3) |
| C(1)-C(2)-C(3)-C(4) | -34.4(3) |
| C(7)-C(2)-C(3)-C(4) | -149.2(2) |
| C(2)-C(3)-C(4)-C(5) | 64.7(4) |
| C(1)-O(2)-C(5)-C(4) | 31.5(6) |
| C(3)-C(4)-C(5)-O(2) | -62.1(5) |
| C(6A)-C(2)-C(3A)-C(4A) | 149.4(6) |
| C(1)-C(2)-C(3A)-C(4A) | 39.4(8) |
| C(7)-C(2)-C(3A)-C(4A) | -91.7(7) |
| C(2)-C(3A)-C(4A)-C(5A) | -64.3(11) |
| C(3A)-C(4A)-C(5A)-O(2) | 63.7(12) |
| C(1)-O(2)-C(5A)-C(4A) | -39.0(12) |
| C(3A)-C(2)-C(7)-O(3) | 69.6(4) |
| C(6A)-C(2)-C(7)-O(3) | -179.76(11) |
| C(6)-C(2)-C(7)-O(3) | -179.76(11) |
| C(1)-C(2)-C(7)-O(3) | -66.24(13) |
| C(3)-C(2)-C(7)-O(3) | 52.47(19) |
| C(3A)-C(2)-C(7)-C(8) | -57.8(5) |
| C(6A)-C(2)-C(7)-C(8) | 52.80(15) |
| C(6)-C(2)-C(7)-C(8) | 52.80(15) |
| C(1)-C(2)-C(7)-C(8) | 166.33(10) |
| C(3)-C(2)-C(7)-C(8) | -75.0(2) |
| O(3)-C(7)-C(8)-C(13) | -41.54(16) |
| C(2)-C(7)-C(8)-C(13) | 82.12(15) |
| O(3)-C(7)-C(8)-C(9) | 137.39(11) |
| C(2)-C(7)-C(8)-C(9) | -98.96(14) |
| C(13)-C(8)-C(9)-C(10) | -5.77(19) |
| C(7)-C(8)-C(9)-C(10) | 175.23(12) |
| C(13)-C(8)-C(9)-C(14) | 171.38(14) |
| C(7)-C(8)-C(9)-C(14) | -7.62(19) |
| C(8)-C(9)-C(10)-C(11) | 2.0(2) |
| C(14)-C(9)-C(10)-C(11) | -175.32(14) |
| C(9)-C(10)-C(11)-C(12) | 2.1(2) |
| C(9)-C(10)-C(11)-C(15) | -179.61(15) |
| C(10)-C(11)-C(12)-C(13) | -2.4(2) |
| C(15)-C(11)-C(12)-C(13) | 179.30(15) |
| C(11)-C(12)-C(13)-C(8) | -1.4(2) |
| C(11)-C(12)-C(13)-C(16) | 175.85(14) |
| C(9)-C(8)-C(13)-C(12) | 5.45(18) |

| | |
|---|---|
| C(7)-C(8)-C(13)-C(12) | -175.63(12) |
| C(9)-C(8)-C(13)-C(16) | -171.55(13) |
| C(7)-C(8)-C(13)-C(16) | 7.4(2) |

Table C.7h Hydrogen bonds for yd6mes [A and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(3)-H(3)...O(1)#1 | 0.91(2) | 1.94(2) | 2.8491(14) | 176.6(19) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y+1/2,-z+3/2

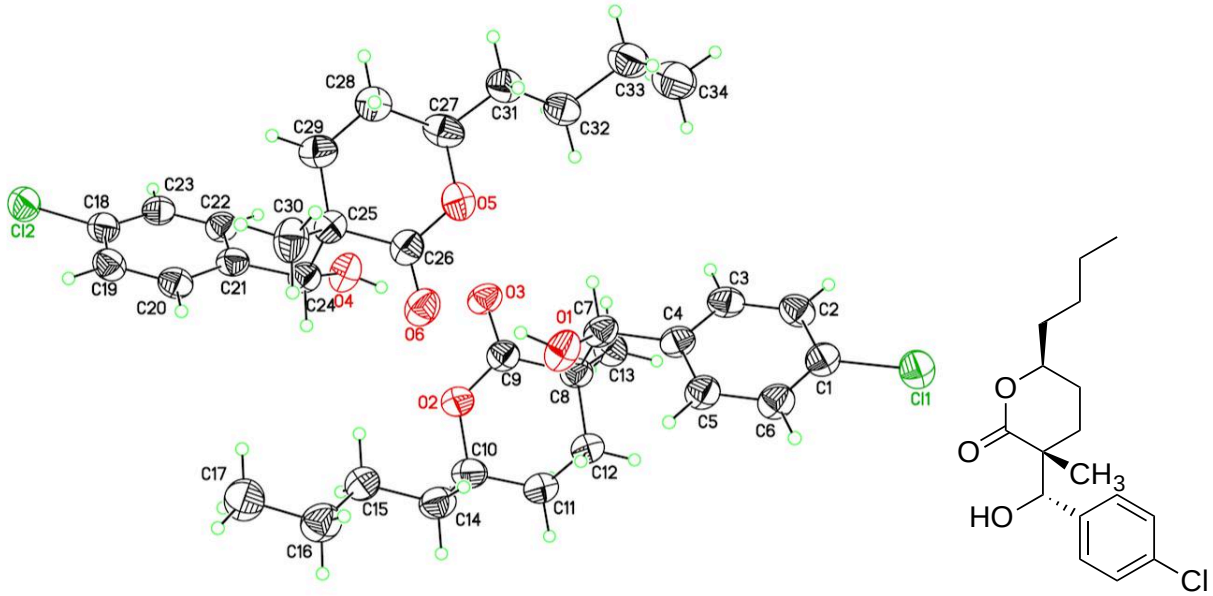



Figure C.9 Structure of yd2cl.

**Structure Determination.**

Colorless needles of **yd2cl** were grown from a dichloromethane/hexanes solution of the compound at 22 deg. C. A crystal of dimensions 0.22 x 0.13 x 0.08 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (ë = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ù. The exposure times were 1 sec. for the low angle images, 8 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 48852 reflections to a maximum 2è value of 139.38° of which 5960 were independent and 5529 were greater than

2ó(I). The final cell constants (Table 1) were based on the xyz centroids 17736 reflections above 10ó(I). Analysis of the data showed negligible decay during data collection. . The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group P2(1)/c with Z = 8 for the formula $C_{17}H_{23}O_3Cl$. There are two independent molecules in the asymmetric unit, one of which exhibits some conformational disorder. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in both refined and idealized positions. Full matrix least-squares refinement based on $F^2$ converged at R1 = 0.0654 and wR2 = 0.1709 [based on I > 2sigma(I)], R1 = 0.0684 and wR2 = 0.1754 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.
Sheldrick, G.M. SHELXTL, v. 2014/6; Bruker Analytical X-ray, Madison, WI, 2014.
CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.
CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015).

Table C.1i Crystal data and structure refinement for yd2cl.

| | |
|---|---|
| Identification code | yd2cl |
| Empirical formula | C17 H23 Cl O3 |
| Formula weight | 310.80 |
| Temperature | 85(2) K |
| Wavelength | 1.54178 A |
| Crystal system, space group | Monoclinic, P2(1)/c |
| Unit cell dimensions | a = 12.6213(3) A alpha = 90 deg.<br>b = 27.0198(6) A beta = 94.797(2) deg.<br>c = 9.4892(2) A gamma = 90 deg. |
| Volume | 3224.72(13) A^3 |
| Z, Calculated density | 8, 1.280 Mg/m^3 |
| Absorption coefficient | 2.157 mm^-1 |
| F(000) | 1328 |
| Crystal size | 0.220 x 0.130 x 0.080 mm |
| Theta range for data collection | 3.271 to 69.689 deg. |
| Limiting indices | -14<=h<=15, -32<=k<=32, -11<=l<=11 |
| Reflections collected / unique | 48852 / 5960 [R(int) = 0.1018] |
| Completeness to theta = 67.679 | 98.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00000 and 0.80425 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 5960 / 140 / 456 |
| Goodness-of-fit on F^2 | 1.022 |
| Final R indices [I>2sigma(I)] | R1 = 0.0654, wR2 = 0.1709 |
| R indices (all data) | R1 = 0.0684, wR2 = 0.1754 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.721 and -0.285 e.A^-3 |

Table C.2i Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for yd2cl. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Cl(1) | -604(1) | 3950(1) | 13558(1) | 48(1) |
| Cl(2) | 7281(1) | 3260(1) | -1132(1) | 53(1) |
| O(1) | 2950(2) | 3793(1) | 8859(2) | 51(1) |
| O(2) | 3492(2) | 4716(1) | 6234(2) | 52(1) |
| O(3) | 2407(1) | 4125(1) | 5578(2) | 45(1) |
| O(4) | 3889(2) | 3886(1) | 3531(2) | 49(1) |
| O(5) | 2904(2) | 3024(1) | 5917(2) | 54(1) |
| O(6) | 4212(2) | 3482(1) | 6775(2) | 49(1) |
| C(1) | 120(2) | 3976(1) | 12068(3) | 42(1) |
| C(2) | -405(2) | 3942(1) | 10729(3) | 44(1) |
| C(3) | 186(2) | 3941(1) | 9562(3) | 44(1) |
| C(4) | 1289(2) | 3988(1) | 9710(3) | 40(1) |
| C(5) | 1789(2) | 4030(1) | 11079(3) | 44(1) |
| C(6) | 1206(2) | 4022(1) | 12250(3) | 45(1) |
| C(7) | 1929(2) | 3983(1) | 8430(3) | 42(1) |
| C(8) | 2026(2) | 4506(1) | 7756(3) | 42(1) |
| C(9) | 2663(2) | 4435(1) | 6471(3) | 41(1) |
| C(10) | 3934(2) | 5107(1) | 7194(3) | 51(1) |
| C(11) | 3113(2) | 5289(1) | 8129(3) | 52(1) |
| C(12) | 2574(2) | 4868(1) | 8840(3) | 48(1) |
| C(13) | 935(2) | 4700(1) | 7169(3) | 47(1) |
| C(14) | 4967(2) | 4914(1) | 7918(3) | 50(1) |
| C(15) | 5747(2) | 4724(1) | 6897(3) | 51(1) |
| C(16) | 6843(3) | 4610(1) | 7547(3) | 60(1) |
| C(17) | 7585(3) | 4407(1) | 6509(4) | 64(1) |
| C(18) | 6579(2) | 3386(1) | 331(3) | 43(1) |
| C(19) | 7096(2) | 3347(1) | 1677(3) | 44(1) |
| C(20) | 6524(2) | 3438(1) | 2832(3) | 43(1) |
| C(21) | 5446(2) | 3551(1) | 2676(3) | 39(1) |
| C(22) | 4956(2) | 3599(1) | 1304(3) | 41(1) |
| C(23) | 5522(2) | 3521(1) | 126(3) | 42(1) |
| C(24) | 4816(2) | 3610(1) | 3955(3) | 40(1) |
| C(25) | 4524(2) | 3096(1) | 4591(3) | 45(1) |
| C(26) | 3860(2) | 3216(1) | 5825(3) | 43(1) |
| C(27) | 2363(5) | 2739(2) | 4690(8) | 50(2) |
| C(28) | 3224(4) | 2415(2) | 4065(5) | 50(1) |
| C(29) | 4012(6) | 2745(4) | 3485(9) | 50(2) |
| C(27A) | 2481(9) | 2609(5) | 5035(12) | 65(3) |
| C(28A) | 2650(7) | 2806(3) | 3571(9) | 61(2) |

| | | | | |
|---|---|---|---|---|
| C(29A) | 3809(10) | 2805(8) | 3459(18) | 72(5) |
| C(30) | 5524(2) | 2835(1) | 5282(3) | 55(1) |
| C(31) | 1489(4) | 2452(2) | 5253(7) | 58(1) |
| C(32) | 629(4) | 2794(2) | 5577(6) | 47(1) |
| C(33) | -371(5) | 2504(2) | 6107(8) | 62(2) |
| C(34) | -1257(8) | 2864(4) | 6152(12) | 74(2) |
| C(31A) | 1251(11) | 2797(8) | 5041(19) | 121(5) |
| C(32A) | 643(12) | 2651(10) | 6120(20) | 161(8) |
| C(33A) | -574(12) | 2602(10) | 5340(20) | 155(8) |
| C(34A) | -1175(19) | 2817(14) | 6470(40) | 183(15) |

Table C.3i Bond lengths [A] and angles [deg] for yd2cl.

| | |
|---|---|
| Cl(1)-C(1) | 1.748(3) |
| Cl(2)-C(18) | 1.742(3) |
| O(1)-C(7) | 1.415(3) |
| O(1)-H(1) | 0.86(4) |
| O(2)-C(9) | 1.328(3) |
| O(2)-C(10) | 1.474(3) |
| O(3)-C(9) | 1.215(3) |
| O(4)-C(24) | 1.418(3) |
| O(4)-H(4) | 0.80(4) |
| O(5)-C(26) | 1.323(3) |
| O(5)-C(27A) | 1.471(11) |
| O(5)-C(27) | 1.511(7) |
| O(6)-C(26) | 1.210(3) |
| C(1)-C(6) | 1.372(4) |
| C(1)-C(2) | 1.386(4) |
| C(2)-C(3) | 1.387(4) |
| C(2)-H(2) | 0.9500 |
| C(3)-C(4) | 1.394(4) |
| C(3)-H(3) | 0.9500 |
| C(4)-C(5) | 1.400(4) |
| C(4)-C(7) | 1.514(4) |
| C(5)-C(6) | 1.383(4) |
| C(5)-H(5) | 0.9500 |
| C(6)-H(6) | 0.9500 |
| C(7)-C(8) | 1.560(4) |
| C(7)-H(7) | 1.0000 |
| C(8)-C(9) | 1.528(4) |
| C(8)-C(13) | 1.533(3) |
| C(8)-C(12) | 1.540(3) |
| C(10)-C(11) | 1.503(4) |
| C(10)-C(14) | 1.515(4) |

| | |
|---|---|
| C(10)-H(10) | 1.0000 |
| C(11)-C(12) | 1.514(4) |
| C(11)-H(11A) | 0.9900 |
| C(11)-H(11B) | 0.9900 |
| C(12)-H(12A) | 0.9900 |
| C(12)-H(12B) | 0.9900 |
| C(13)-H(13A) | 0.9800 |
| C(13)-H(13B) | 0.9800 |
| C(13)-H(13C) | 0.9800 |
| C(14)-C(15) | 1.526(4) |
| C(14)-H(14A) | 0.9900 |
| C(14)-H(14B) | 0.9900 |
| C(15)-C(16) | 1.500(4) |
| C(15)-H(15A) | 0.9900 |
| C(15)-H(15B) | 0.9900 |
| C(16)-C(17) | 1.517(5) |
| C(16)-H(16A) | 0.9900 |
| C(16)-H(16B) | 0.9900 |
| C(17)-H(17A) | 0.9800 |
| C(17)-H(17B) | 0.9800 |
| C(17)-H(17C) | 0.9800 |
| C(18)-C(23) | 1.381(4) |
| C(18)-C(19) | 1.388(4) |
| C(19)-C(20) | 1.384(4) |
| C(19)-H(19) | 0.9500 |
| C(20)-C(21) | 1.391(4) |
| C(20)-H(20) | 0.9500 |
| C(21)-C(22) | 1.400(3) |
| C(21)-C(24) | 1.514(4) |
| C(22)-C(23) | 1.392(4) |
| C(22)-H(22) | 0.9500 |
| C(23)-H(23) | 0.9500 |
| C(24)-C(25) | 1.569(4) |
| C(24)-H(24) | 1.0000 |
| C(25)-C(29) | 1.519(8) |
| C(25)-C(26) | 1.530(4) |
| C(25)-C(30) | 1.544(4) |
| C(25)-C(29A) | 1.557(12) |
| C(27)-C(31) | 1.484(8) |
| C(27)-C(28) | 1.552(8) |
| C(27)-H(27A) | 1.0000 |
| C(28)-C(29) | 1.476(10) |
| C(28)-H(28A) | 0.9900 |
| C(28)-H(28B) | 0.9900 |
| C(29)-H(29A) | 0.9900 |
| C(29)-H(29B) | 0.9900 |

| | |
|---|---|
| C(27A)-C(28A) | 1.518(12) |
| C(27A)-C(31A) | 1.63(2) |
| C(27A)-H(27B) | 1.0000 |
| C(28A)-C(29A) | 1.476(14) |
| C(28A)-H(28C) | 0.9900 |
| C(28A)-H(28D) | 0.9900 |
| C(29A)-H(29C) | 0.9900 |
| C(29A)-H(29D) | 0.9900 |
| C(30)-H(30A) | 0.9800 |
| C(30)-H(30B) | 0.9800 |
| C(30)-H(30C) | 0.9800 |
| C(31)-C(32) | 1.478(7) |
| C(31)-H(31A) | 0.9900 |
| C(31)-H(31B) | 0.9900 |
| C(32)-C(33) | 1.603(8) |
| C(32)-H(32A) | 0.9900 |
| C(32)-H(32B) | 0.9900 |
| C(33)-C(34) | 1.485(9) |
| C(33)-H(33A) | 0.9900 |
| C(33)-H(33B) | 0.9900 |
| C(34)-H(34A) | 0.9800 |
| C(34)-H(34B) | 0.9800 |
| C(34)-H(34C) | 0.9800 |
| C(31A)-C(32A) | 1.383(15) |
| C(31A)-H(31C) | 0.9900 |
| C(31A)-H(31D) | 0.9900 |
| C(32A)-C(33A) | 1.654(17) |
| C(32A)-H(32C) | 0.9900 |
| C(32A)-H(32D) | 0.9900 |
| C(33A)-C(34A) | 1.484(17) |
| C(33A)-H(33C) | 0.9900 |
| C(33A)-H(33D) | 0.9900 |
| C(34A)-H(34E) | 0.9800 |
| C(34A)-H(34F) | 0.9800 |
| C(34A)-H(34G) | 0.9800 |
| C(7)-O(1)-H(1) | 113(3) |
| C(9)-O(2)-C(10) | 124.7(2) |
| C(24)-O(4)-H(4) | 108(2) |
| C(26)-O(5)-C(27A) | 123.4(5) |
| C(26)-O(5)-C(27) | 120.3(3) |
| C(6)-C(1)-C(2) | 121.2(3) |
| C(6)-C(1)-Cl(1) | 119.1(2) |
| C(2)-C(1)-Cl(1) | 119.7(2) |
| C(1)-C(2)-C(3) | 119.0(2) |
| C(1)-C(2)-H(2) | 120.5 |
| C(3)-C(2)-H(2) | 120.5 |

| | |
|---|---|
| C(2)-C(3)-C(4) | 121.2(2) |
| C(2)-C(3)-H(3) | 119.4 |
| C(4)-C(3)-H(3) | 119.4 |
| C(3)-C(4)-C(5) | 118.0(3) |
| C(3)-C(4)-C(7) | 120.9(2) |
| C(5)-C(4)-C(7) | 121.1(2) |
| C(6)-C(5)-C(4) | 121.0(2) |
| C(6)-C(5)-H(5) | 119.5 |
| C(4)-C(5)-H(5) | 119.5 |
| C(1)-C(6)-C(5) | 119.5(2) |
| C(1)-C(6)-H(6) | 120.2 |
| C(5)-C(6)-H(6) | 120.2 |
| O(1)-C(7)-C(4) | 107.8(2) |
| O(1)-C(7)-C(8) | 110.2(2) |
| C(4)-C(7)-C(8) | 112.7(2) |
| O(1)-C(7)-H(7) | 108.7 |
| C(4)-C(7)-H(7) | 108.7 |
| C(8)-C(7)-H(7) | 108.7 |
| C(9)-C(8)-C(13) | 105.6(2) |
| C(9)-C(8)-C(12) | 112.1(2) |
| C(13)-C(8)-C(12) | 111.5(2) |
| C(9)-C(8)-C(7) | 106.1(2) |
| C(13)-C(8)-C(7) | 111.1(2) |
| C(12)-C(8)-C(7) | 110.3(2) |
| O(3)-C(9)-O(2) | 116.3(2) |
| O(3)-C(9)-C(8) | 121.1(2) |
| O(2)-C(9)-C(8) | 122.5(2) |
| O(2)-C(10)-C(11) | 110.8(2) |
| O(2)-C(10)-C(14) | 107.4(2) |
| C(11)-C(10)-C(14) | 117.1(2) |
| O(2)-C(10)-H(10) | 107.0 |
| C(11)-C(10)-H(10) | 107.0 |
| C(14)-C(10)-H(10) | 107.0 |
| C(10)-C(11)-C(12) | 112.0(2) |
| C(10)-C(11)-H(11A) | 109.2 |
| C(12)-C(11)-H(11A) | 109.2 |
| C(10)-C(11)-H(11B) | 109.2 |
| C(12)-C(11)-H(11B) | 109.2 |
| H(11A)-C(11)-H(11B) | 107.9 |
| C(11)-C(12)-C(8) | 111.9(2) |
| C(11)-C(12)-H(12A) | 109.2 |
| C(8)-C(12)-H(12A) | 109.2 |
| C(11)-C(12)-H(12B) | 109.2 |
| C(8)-C(12)-H(12B) | 109.2 |
| H(12A)-C(12)-H(12B) | 107.9 |
| C(8)-C(13)-H(13A) | 109.5 |

| | |
|---|---|
| C(8)-C(13)-H(13B) | 109.5 |
| H(13A)-C(13)-H(13B) | 109.5 |
| C(8)-C(13)-H(13C) | 109.5 |
| H(13A)-C(13)-H(13C) | 109.5 |
| H(13B)-C(13)-H(13C) | 109.5 |
| C(10)-C(14)-C(15) | 113.8(2) |
| C(10)-C(14)-H(14A) | 108.8 |
| C(15)-C(14)-H(14A) | 108.8 |
| C(10)-C(14)-H(14B) | 108.8 |
| C(15)-C(14)-H(14B) | 108.8 |
| H(14A)-C(14)-H(14B) | 107.7 |
| C(16)-C(15)-C(14) | 115.5(2) |
| C(16)-C(15)-H(15A) | 108.4 |
| C(14)-C(15)-H(15A) | 108.4 |
| C(16)-C(15)-H(15B) | 108.4 |
| C(14)-C(15)-H(15B) | 108.4 |
| H(15A)-C(15)-H(15B) | 107.5 |
| C(15)-C(16)-C(17) | 113.9(3) |
| C(15)-C(16)-H(16A) | 108.8 |
| C(17)-C(16)-H(16A) | 108.8 |
| C(15)-C(16)-H(16B) | 108.8 |
| C(17)-C(16)-H(16B) | 108.8 |
| H(16A)-C(16)-H(16B) | 107.7 |
| C(16)-C(17)-H(17A) | 109.5 |
| C(16)-C(17)-H(17B) | 109.5 |
| H(17A)-C(17)-H(17B) | 109.5 |
| C(16)-C(17)-H(17C) | 109.5 |
| H(17A)-C(17)-H(17C) | 109.5 |
| H(17B)-C(17)-H(17C) | 109.5 |
| C(23)-C(18)-C(19) | 121.6(3) |
| C(23)-C(18)-Cl(2) | 119.2(2) |
| C(19)-C(18)-Cl(2) | 119.2(2) |
| C(20)-C(19)-C(18) | 118.6(2) |
| C(20)-C(19)-H(19) | 120.7 |
| C(18)-C(19)-H(19) | 120.7 |
| C(19)-C(20)-C(21) | 121.7(2) |
| C(19)-C(20)-H(20) | 119.2 |
| C(21)-C(20)-H(20) | 119.2 |
| C(20)-C(21)-C(22) | 118.1(2) |
| C(20)-C(21)-C(24) | 120.8(2) |
| C(22)-C(21)-C(24) | 121.1(2) |
| C(23)-C(22)-C(21) | 121.1(2) |
| C(23)-C(22)-H(22) | 119.5 |
| C(21)-C(22)-H(22) | 119.5 |
| C(18)-C(23)-C(22) | 118.7(2) |
| C(18)-C(23)-H(23) | 120.6 |

| | |
|---|---|
| C(22)-C(23)-H(23) | 120.6 |
| O(4)-C(24)-C(21) | 107.7(2) |
| O(4)-C(24)-C(25) | 111.1(2) |
| C(21)-C(24)-C(25) | 111.8(2) |
| O(4)-C(24)-H(24) | 108.7 |
| C(21)-C(24)-H(24) | 108.7 |
| C(25)-C(24)-H(24) | 108.7 |
| C(29)-C(25)-C(26) | 115.6(4) |
| C(29)-C(25)-C(30) | 107.0(4) |
| C(26)-C(25)-C(30) | 104.6(2) |
| C(26)-C(25)-C(29A) | 108.2(5) |
| C(30)-C(25)-C(29A) | 117.9(9) |
| C(29)-C(25)-C(24) | 112.8(4) |
| C(26)-C(25)-C(24) | 105.6(2) |
| C(30)-C(25)-C(24) | 110.9(2) |
| C(29A)-C(25)-C(24) | 108.8(9) |
| O(6)-C(26)-O(5) | 117.7(2) |
| O(6)-C(26)-C(25) | 120.4(2) |
| O(5)-C(26)-C(25) | 121.9(2) |
| C(31)-C(27)-O(5) | 106.9(5) |
| C(31)-C(27)-C(28) | 114.1(5) |
| O(5)-C(27)-C(28) | 107.2(4) |
| C(31)-C(27)-H(27A) | 109.5 |
| O(5)-C(27)-H(27A) | 109.5 |
| C(28)-C(27)-H(27A) | 109.5 |
| C(29)-C(28)-C(27) | 108.5(5) |
| C(29)-C(28)-H(28A) | 110.0 |
| C(27)-C(28)-H(28A) | 110.0 |
| C(29)-C(28)-H(28B) | 110.0 |
| C(27)-C(28)-H(28B) | 110.0 |
| H(28A)-C(28)-H(28B) | 108.4 |
| C(28)-C(29)-C(25) | 112.4(6) |
| C(28)-C(29)-H(29A) | 109.1 |
| C(25)-C(29)-H(29A) | 109.1 |
| C(28)-C(29)-H(29B) | 109.1 |
| C(25)-C(29)-H(29B) | 109.1 |
| H(29A)-C(29)-H(29B) | 107.9 |
| O(5)-C(27A)-C(28A) | 100.5(8) |
| O(5)-C(27A)-C(31A) | 93.5(11) |
| C(28A)-C(27A)-C(31A) | 95.8(10) |
| O(5)-C(27A)-H(27B) | 120.4 |
| C(28A)-C(27A)-H(27B) | 120.4 |
| C(31A)-C(27A)-H(27B) | 120.4 |
| C(29A)-C(28A)-C(27A) | 106.3(10) |
| C(29A)-C(28A)-H(28C) | 110.5 |
| C(27A)-C(28A)-H(28C) | 110.5 |

| | |
|---|---|
| C(29A)-C(28A)-H(28D) | 110.5 |
| C(27A)-C(28A)-H(28D) | 110.5 |
| H(28C)-C(28A)-H(28D) | 108.7 |
| C(28A)-C(29A)-C(25) | 118.1(10) |
| C(28A)-C(29A)-H(29C) | 107.8 |
| C(25)-C(29A)-H(29C) | 107.8 |
| C(28A)-C(29A)-H(29D) | 107.8 |
| C(25)-C(29A)-H(29D) | 107.8 |
| H(29C)-C(29A)-H(29D) | 107.1 |
| C(25)-C(30)-H(30A) | 109.5 |
| C(25)-C(30)-H(30B) | 109.5 |
| H(30A)-C(30)-H(30B) | 109.5 |
| C(25)-C(30)-H(30C) | 109.5 |
| H(30A)-C(30)-H(30C) | 109.5 |
| H(30B)-C(30)-H(30C) | 109.5 |
| C(32)-C(31)-C(27) | 109.2(5) |
| C(32)-C(31)-H(31A) | 109.8 |
| C(27)-C(31)-H(31A) | 109.8 |
| C(32)-C(31)-H(31B) | 109.8 |
| C(27)-C(31)-H(31B) | 109.8 |
| H(31A)-C(31)-H(31B) | 108.3 |
| C(31)-C(32)-C(33) | 111.7(4) |
| C(31)-C(32)-H(32A) | 109.3 |
| C(33)-C(32)-H(32A) | 109.3 |
| C(31)-C(32)-H(32B) | 109.3 |
| C(33)-C(32)-H(32B) | 109.3 |
| H(32A)-C(32)-H(32B) | 107.9 |
| C(34)-C(33)-C(32) | 107.6(6) |
| C(34)-C(33)-H(33A) | 110.2 |
| C(32)-C(33)-H(33A) | 110.2 |
| C(34)-C(33)-H(33B) | 110.2 |
| C(32)-C(33)-H(33B) | 110.2 |
| H(33A)-C(33)-H(33B) | 108.5 |
| C(33)-C(34)-H(34A) | 109.5 |
| C(33)-C(34)-H(34B) | 109.5 |
| H(34A)-C(34)-H(34B) | 109.5 |
| C(33)-C(34)-H(34C) | 109.5 |
| H(34A)-C(34)-H(34C) | 109.5 |
| H(34B)-C(34)-H(34C) | 109.5 |
| C(32A)-C(31A)-C(27A) | 120.0(15) |
| C(32A)-C(31A)-H(31C) | 107.3 |
| C(27A)-C(31A)-H(31C) | 107.3 |
| C(32A)-C(31A)-H(31D) | 107.3 |
| C(27A)-C(31A)-H(31D) | 107.3 |
| H(31C)-C(31A)-H(31D) | 106.9 |
| C(31A)-C(32A)-C(33A) | 104.2(15) |

| | |
|---|---|
| C(31A)-C(32A)-H(32C) | 110.9 |
| C(33A)-C(32A)-H(32C) | 110.9 |
| C(31A)-C(32A)-H(32D) | 110.9 |
| C(33A)-C(32A)-H(32D) | 110.9 |
| H(32C)-C(32A)-H(32D) | 108.9 |
| C(34A)-C(33A)-C(32A) | 99.0(16) |
| C(34A)-C(33A)-H(33C) | 112.0 |
| C(32A)-C(33A)-H(33C) | 112.0 |
| C(34A)-C(33A)-H(33D) | 112.0 |
| C(32A)-C(33A)-H(33D) | 112.0 |
| H(33C)-C(33A)-H(33D) | 109.6 |
| C(33A)-C(34A)-H(34E) | 109.5 |
| C(33A)-C(34A)-H(34F) | 109.5 |
| H(34E)-C(34A)-H(34F) | 109.5 |
| C(33A)-C(34A)-H(34G) | 109.5 |
| H(34E)-C(34A)-H(34G) | 109.5 |
| H(34F)-C(34A)-H(34G) | 109.5 |

Table C.4i Anisotropic displacement parameters (A^2 x 10^3) for yd2cl. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Cl(1) | 44(1) | 56(1) | 43(1) | 6(1) | 1(1) | 1(1) |
| Cl(2) | 48(1) | 65(1) | 45(1) | -7(1) | 7(1) | -5(1) |
| O(1) | 48(1) | 67(1) | 36(1) | -3(1) | -3(1) | 18(1) |
| O(2) | 52(1) | 61(1) | 43(1) | -13(1) | 6(1) | -13(1) |
| O(3) | 45(1) | 51(1) | 37(1) | -9(1) | -7(1) | 4(1) |
| O(4) | 48(1) | 63(1) | 36(1) | 1(1) | -1(1) | 18(1) |
| O(5) | 42(1) | 61(1) | 60(1) | -5(1) | 10(1) | -1(1) |
| O(6) | 47(1) | 58(1) | 42(1) | -6(1) | 0(1) | 9(1) |
| C(1) | 44(1) | 42(1) | 38(1) | 1(1) | 0(1) | 2(1) |
| C(2) | 39(1) | 50(1) | 43(1) | 4(1) | -6(1) | -5(1) |
| C(3) | 44(1) | 47(1) | 39(1) | 0(1) | -10(1) | -4(1) |
| C(4) | 42(1) | 42(1) | 36(1) | -2(1) | -5(1) | 2(1) |
| C(5) | 37(1) | 54(2) | 39(1) | -5(1) | -5(1) | 4(1) |
| C(6) | 41(1) | 54(2) | 39(1) | -3(1) | -6(1) | 5(1) |
| C(7) | 41(1) | 47(1) | 36(1) | -7(1) | -5(1) | 5(1) |
| C(8) | 37(1) | 46(1) | 41(1) | -6(1) | -3(1) | 0(1) |
| C(9) | 38(1) | 47(1) | 37(1) | -2(1) | -5(1) | 3(1) |
| C(10) | 54(2) | 50(2) | 47(2) | -8(1) | 2(1) | -10(1) |
| C(11) | 53(2) | 53(2) | 50(2) | -12(1) | 3(1) | -6(1) |
| C(12) | 48(2) | 53(2) | 43(1) | -11(1) | 4(1) | -7(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(13) | 41(1) | 48(1) | 52(2) | 4(1) | 0(1) | 4(1) |
| C(14) | 55(2) | 52(2) | 44(2) | -7(1) | -1(1) | -4(1) |
| C(15) | 53(2) | 58(2) | 42(1) | -6(1) | 4(1) | -4(1) |
| C(16) | 61(2) | 69(2) | 48(2) | -4(1) | -4(1) | 4(2) |
| C(17) | 55(2) | 81(2) | 56(2) | -4(2) | -3(1) | 7(2) |
| C(18) | 44(1) | 45(1) | 41(1) | -3(1) | 4(1) | -6(1) |
| C(19) | 38(1) | 49(1) | 44(1) | 0(1) | 0(1) | -4(1) |
| C(20) | 40(1) | 47(1) | 41(1) | -1(1) | -4(1) | -3(1) |
| C(21) | 39(1) | 39(1) | 39(1) | -4(1) | -3(1) | -2(1) |
| C(22) | 40(1) | 44(1) | 38(1) | -3(1) | -3(1) | 1(1) |
| C(23) | 43(1) | 46(1) | 37(1) | -4(1) | -3(1) | -3(1) |
| C(24) | 38(1) | 44(1) | 36(1) | -3(1) | -5(1) | 3(1) |
| C(25) | 45(1) | 46(1) | 43(1) | -8(1) | 6(1) | -1(1) |
| C(26) | 40(1) | 46(1) | 41(1) | 0(1) | 0(1) | 8(1) |
| C(27) | 40(2) | 42(3) | 66(4) | 5(2) | -12(2) | 0(2) |
| C(28) | 49(2) | 48(2) | 51(3) | -2(2) | 3(2) | -3(2) |
| C(29) | 53(3) | 41(3) | 54(3) | -3(2) | -2(3) | 0(3) |
| C(27A) | 57(5) | 81(7) | 56(5) | 2(4) | -7(4) | -14(5) |
| C(28A) | 67(4) | 71(5) | 44(4) | 2(3) | -3(3) | -19(4) |
| C(29A) | 71(6) | 86(11) | 60(6) | -31(6) | 14(4) | -29(6) |
| C(30) | 55(2) | 53(2) | 58(2) | 9(1) | 14(1) | 13(1) |
| C(31) | 54(3) | 44(3) | 78(4) | -9(2) | 16(2) | -7(2) |
| C(32) | 51(3) | 40(2) | 51(3) | 5(2) | 0(2) | -4(2) |
| C(33) | 49(3) | 54(3) | 82(4) | -7(3) | 2(3) | -7(2) |
| C(34) | 58(4) | 59(4) | 103(6) | -8(4) | 4(4) | -2(3) |
| C(31A) | 57(5) | 155(13) | 150(10) | 36(9) | 11(5) | -9(6) |
| C(32A) | 91(8) | 190(20) | 210(14) | 28(12) | 66(9) | -29(9) |
| C(33A) | 88(8) | 175(19) | 211(18) | -50(15) | 64(9) | -16(9) |
| C(34A) | 86(12) | 230(30) | 240(30) | -120(20) | 64(14) | -64(13) |

Table C.5i Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for yd2cl.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 3280(30) | 3683(16) | 8170(50) | 80(13) |
| H(4) | 3610(30) | 3964(12) | 4230(40) | 51(9) |
| H(2) | -1158 | 3918 | 10614 | 53 |
| H(3) | -168 | 3908 | 8643 | 53 |
| H(5) | 2540 | 4063 | 11205 | 52 |
| H(6) | 1554 | 4049 | 13174 | 54 |
| H(7) | 1574 | 3756 | 7704 | 50 |
| H(10) | 4120 | 5392 | 6589 | 61 |

| | | | | |
|---|---|---|---|---|
| H(11A) | 2570 | 5484 | 7555 | 62 |
| H(11B) | 3457 | 5511 | 8861 | 62 |
| H(12A) | 2039 | 5004 | 9439 | 58 |
| H(12B) | 3110 | 4686 | 9461 | 58 |
| H(13A) | 1028 | 5003 | 6623 | 71 |
| H(13B) | 501 | 4772 | 7953 | 71 |
| H(13C) | 579 | 4449 | 6553 | 71 |
| H(14A) | 4804 | 4641 | 8563 | 61 |
| H(14B) | 5312 | 5182 | 8500 | 61 |
| H(15A) | 5447 | 4421 | 6436 | 61 |
| H(15B) | 5804 | 4976 | 6148 | 61 |
| H(16A) | 6789 | 4366 | 8316 | 72 |
| H(16B) | 7158 | 4916 | 7975 | 72 |
| H(17A) | 7287 | 4100 | 6089 | 96 |
| H(17B) | 8281 | 4338 | 7006 | 96 |
| H(17C) | 7665 | 4650 | 5760 | 96 |
| H(19) | 7827 | 3260 | 1802 | 52 |
| H(20) | 6877 | 3423 | 3755 | 51 |
| H(22) | 4226 | 3687 | 1174 | 49 |
| H(23) | 5188 | 3560 | -802 | 51 |
| H(24) | 5254 | 3801 | 4695 | 47 |
| H(27A) | 2059 | 2976 | 3954 | 60 |
| H(28A) | 3577 | 2202 | 4812 | 60 |
| H(28B) | 2893 | 2199 | 3308 | 60 |
| H(29A) | 3657 | 2940 | 2698 | 60 |
| H(29B) | 4572 | 2542 | 3097 | 60 |
| H(27B) | 2676 | 2261 | 5296 | 78 |
| H(28C) | 2288 | 2592 | 2834 | 73 |
| H(28D) | 2362 | 3146 | 3453 | 73 |
| H(29C) | 3940 | 2940 | 2519 | 86 |
| H(29D) | 4051 | 2457 | 3482 | 86 |
| H(30A) | 5310 | 2549 | 5825 | 82 |
| H(30B) | 5928 | 3067 | 5915 | 82 |
| H(30C) | 5968 | 2724 | 4544 | 82 |
| H(31A) | 1211 | 2205 | 4546 | 70 |
| H(31B) | 1759 | 2273 | 6122 | 70 |
| H(32A) | 398 | 2987 | 4719 | 57 |
| H(32B) | 904 | 3030 | 6319 | 57 |
| H(33A) | -582 | 2230 | 5450 | 74 |
| H(33B) | -188 | 2363 | 7060 | 74 |
| H(34A) | -1038 | 3135 | 6801 | 110 |
| H(34B) | -1879 | 2697 | 6482 | 110 |
| H(34C) | -1436 | 2998 | 5202 | 110 |
| H(31C) | 1261 | 3163 | 5033 | 145 |
| H(31D) | 871 | 2690 | 4137 | 145 |
| H(32C) | 671 | 2902 | 6879 | 193 |

| | | | | |
|---|---|---|---|---|
| H(32D) | 893 | 2330 | 6520 | 193 |
| H(33C) | -666 | 2798 | 4452 | 186 |
| H(33D) | -774 | 2253 | 5135 | 186 |
| H(34E) | -936 | 2664 | 7376 | 274 |
| H(34F) | -1936 | 2753 | 6254 | 274 |
| H(34G) | -1051 | 3175 | 6521 | 274 |

Table C.6i Torsion angles [deg] for yd2cl.

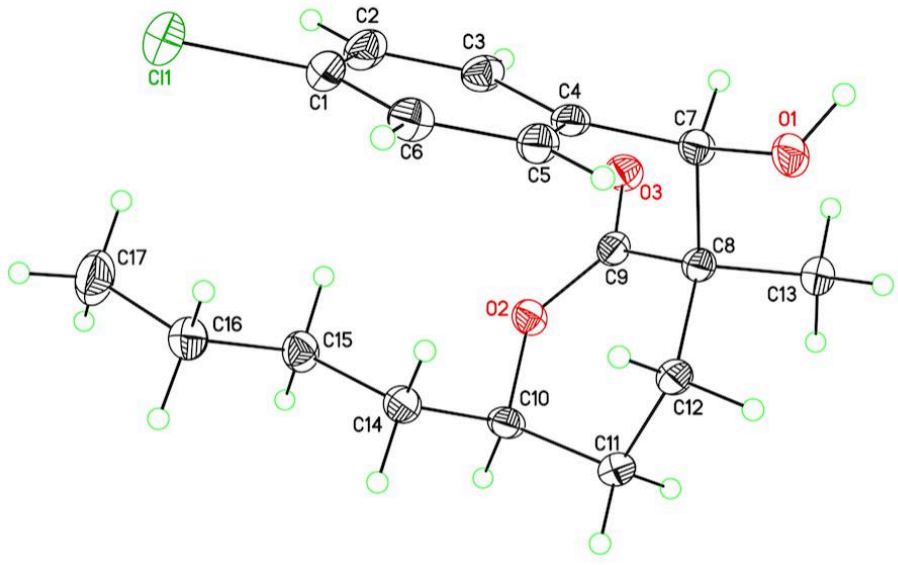
| | |
|---|---|
| C(6)-C(1)-C(2)-C(3) | 1.7(4) |
| Cl(1)-C(1)-C(2)-C(3) | -177.2(2) |
| C(1)-C(2)-C(3)-C(4) | -1.7(4) |
| C(2)-C(3)-C(4)-C(5) | 0.8(4) |
| C(2)-C(3)-C(4)-C(7) | 179.5(2) |
| C(3)-C(4)-C(5)-C(6) | 0.3(4) |
| C(7)-C(4)-C(5)-C(6) | -178.5(2) |
| C(2)-C(1)-C(6)-C(5) | -0.6(4) |
| Cl(1)-C(1)-C(6)-C(5) | 178.2(2) |
| C(4)-C(5)-C(6)-C(1) | -0.3(4) |
| C(3)-C(4)-C(7)-O(1) | -151.4(2) |
| C(5)-C(4)-C(7)-O(1) | 27.3(3) |
| C(3)-C(4)-C(7)-C(8) | 86.7(3) |
| C(5)-C(4)-C(7)-C(8) | -94.6(3) |
| O(1)-C(7)-C(8)-C(9) | 60.8(2) |
| C(4)-C(7)-C(8)-C(9) | -178.63(19) |
| O(1)-C(7)-C(8)-C(13) | 175.1(2) |
| C(4)-C(7)-C(8)-C(13) | -64.3(3) |
| O(1)-C(7)-C(8)-C(12) | -60.8(3) |
| C(4)-C(7)-C(8)-C(12) | 59.8(3) |
| C(10)-O(2)-C(9)-O(3) | -179.2(2) |
| C(10)-O(2)-C(9)-C(8) | 3.5(4) |
| C(13)-C(8)-C(9)-O(3) | -65.9(3) |
| C(12)-C(8)-C(9)-O(3) | 172.4(2) |
| C(7)-C(8)-C(9)-O(3) | 52.0(3) |
| C(13)-C(8)-C(9)-O(2) | 111.3(3) |
| C(12)-C(8)-C(9)-O(2) | -10.4(3) |
| C(7)-C(8)-C(9)-O(2) | -130.8(2) |
| C(9)-O(2)-C(10)-C(11) | -23.1(4) |
| C(9)-O(2)-C(10)-C(14) | 105.9(3) |
| O(2)-C(10)-C(11)-C(12) | 49.9(3) |
| C(14)-C(10)-C(11)-C(12) | -73.7(3) |
| C(10)-C(11)-C(12)-C(8) | -58.6(3) |
| C(9)-C(8)-C(12)-C(11) | 37.0(3) |
| C(13)-C(8)-C(12)-C(11) | -81.2(3) |

| | |
|---|---|
| C(7)-C(8)-C(12)-C(11) | 155.0(2) |
| O(2)-C(10)-C(14)-C(15) | 53.3(3) |
| C(11)-C(10)-C(14)-C(15) | 178.6(2) |
| C(10)-C(14)-C(15)-C(16) | 170.1(3) |
| C(14)-C(15)-C(16)-C(17) | 178.0(3) |
| C(23)-C(18)-C(19)-C(20) | 1.3(4) |
| Cl(2)-C(18)-C(19)-C(20) | -178.7(2) |
| C(18)-C(19)-C(20)-C(21) | 2.0(4) |
| C(19)-C(20)-C(21)-C(22) | -3.6(4) |
| C(19)-C(20)-C(21)-C(24) | 175.2(2) |
| C(20)-C(21)-C(22)-C(23) | 2.0(4) |
| C(24)-C(21)-C(22)-C(23) | -176.8(2) |
| C(19)-C(18)-C(23)-C(22) | -2.8(4) |
| Cl(2)-C(18)-C(23)-C(22) | 177.2(2) |
| C(21)-C(22)-C(23)-C(18) | 1.1(4) |
| C(20)-C(21)-C(24)-O(4) | 159.7(2) |
| C(22)-C(21)-C(24)-O(4) | -21.5(3) |
| C(20)-C(21)-C(24)-C(25) | -78.0(3) |
| C(22)-C(21)-C(24)-C(25) | 100.8(3) |
| O(4)-C(24)-C(25)-C(29) | 69.6(4) |
| C(21)-C(24)-C(25)-C(29) | -50.7(4) |
| O(4)-C(24)-C(25)-C(26) | -57.5(3) |
| C(21)-C(24)-C(25)-C(26) | -177.85(19) |
| O(4)-C(24)-C(25)-C(30) | -170.3(2) |
| C(21)-C(24)-C(25)-C(30) | 69.4(3) |
| O(4)-C(24)-C(25)-C(29A) | 58.4(7) |
| C(21)-C(24)-C(25)-C(29A) | -61.9(7) |
| C(27A)-O(5)-C(26)-O(6) | -165.3(7) |
| C(27)-O(5)-C(26)-O(6) | 172.6(3) |
| C(27A)-O(5)-C(26)-C(25) | 12.8(7) |
| C(27)-O(5)-C(26)-C(25) | -9.3(4) |
| C(29)-C(25)-C(26)-O(6) | 178.2(5) |
| C(30)-C(25)-C(26)-O(6) | 60.8(3) |
| C(29A)-C(25)-C(26)-O(6) | -172.8(10) |
| C(24)-C(25)-C(26)-O(6) | -56.4(3) |
| C(29)-C(25)-C(26)-O(5) | 0.1(6) |
| C(30)-C(25)-C(26)-O(5) | -117.3(3) |
| C(29A)-C(25)-C(26)-O(5) | 9.1(10) |
| C(24)-C(25)-C(26)-O(5) | 125.5(2) |
| C(26)-O(5)-C(27)-C(31) | 163.4(4) |
| C(26)-O(5)-C(27)-C(28) | 40.6(5) |
| C(31)-C(27)-C(28)-C(29) | 177.3(6) |
| O(5)-C(27)-C(28)-C(29) | -64.5(6) |
| C(27)-C(28)-C(29)-C(25) | 57.9(7) |
| C(26)-C(25)-C(29)-C(28) | -25.7(8) |
| C(30)-C(25)-C(29)-C(28) | 90.4(6) |

| | |
|---|---|
| C(24)-C(25)-C(29)-C(28) | -147.4(5) |
| C(26)-O(5)-C(27A)-C(28A) | -52.8(10) |
| C(26)-O(5)-C(27A)-C(31A) | -149.3(6) |
| O(5)-C(27A)-C(28A)-C(29A) | 69.9(12) |
| C(31A)-C(27A)-C(28A)-C(29A) | 164.6(12) |
| C(27A)-C(28A)-C(29A)-C(25) | -56.4(19) |
| C(26)-C(25)-C(29A)-C(28A) | 14.5(19) |
| C(30)-C(25)-C(29A)-C(28A) | 132.8(14) |
| C(24)-C(25)-C(29A)-C(28A) | -99.8(15) |
| O(5)-C(27)-C(31)-C(32) | 71.8(6) |
| C(28)-C(27)-C(31)-C(32) | -169.8(5) |
| C(27)-C(31)-C(32)-C(33) | 176.7(5) |
| C(31)-C(32)-C(33)-C(34) | -169.8(7) |
| O(5)-C(27A)-C(31A)-C(32A) | -88(2) |
| C(28A)-C(27A)-C(31A)-C(32A) | 171.5(19) |
| C(27A)-C(31A)-C(32A)-C(33A) | -146.3(17) |
| C(31A)-C(32A)-C(33A)-C(34A) | -140(3) |

Table C.7i Hydrogen bonds for yd2cl [A and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(1)-H(1)...O(6) | 0.86(4) | 1.92(4) | 2.771(3) | 171(4) |
| O(4)-H(4)...O(3) | 0.80(4) | 2.11(4) | 2.880(3) | 160(3) |



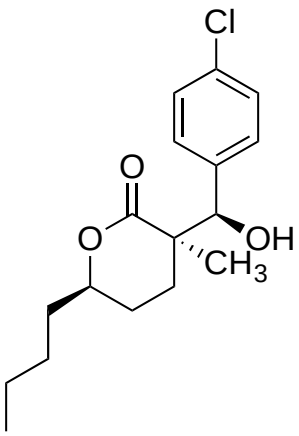




Figure C.10 Structure of yd1cl.

**Structure Determination.**

Colorless plates of **yd1cl** were grown from a dichloromethane/hexanes solution of the compound at 22 deg. C. A crystal of dimensions 0.21 x 0.16 x 0.16 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (ë = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ù. The exposure times were 1 sec. for the low angle images, 8 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 22619 reflections to a maximum 2è value of 138.87° of which 2895 were independent and 2860 were greater than 2ó(I). The final cell constants (Table 1) were based on the xyz centroids 13845 reflections above 10ó(I). Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group P2(1)/c with Z = 4 for the formula $C_{17}H_{23}O_3Cl$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in a combination of idealized and refined positions. Full matrix least-squares refinement based on $F^2$ converged at R1 = 0.0358 and wR2 = 0.0960 [based on I > 2sigma(I)], R1 = 0.0360 and wR2 = 0.0962 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Sheldrick, G.M. SHELXTL, v. 2014/6; Bruker Analytical X-ray, Madison, WI, 2014.
CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.
CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015).

Table C.1j Crystal data and structure refinement for yd1cl.

| | |
|---|---|
| Identification code | yd1cl |
| Empirical formula | C17 H23 Cl O3 |
| Formula weight | 310.80 |
| Temperature | 85(2) K |
| Wavelength | 1.54178 A |
| Crystal system, space group | Monoclinic, P2(1)/c |
| Unit cell dimensions | a = 16.56663(18) A alpha = 90 deg.<br>b = 6.87384(5) A beta = 114.3724(14) deg.<br>c = 15.21522(19) A gamma = 90 deg. |
| Volume | 1578.24(3) A^3 |
| Z, Calculated density | 4, 1.308 Mg/m^3 |
| Absorption coefficient | 2.204 mm^-1 |
| F(000) | 664 |
| Crystal size | 0.210 x 0.160 x 0.160 mm |
| Theta range for data collection | 2.928 to 69.437 deg. |
| Limiting indices | -20<=h<=19, -8<=k<=8, -17<=l<=18 |
| Reflections collected / unique | 22619 / 2895 [R(int) = 0.0392] |
| Completeness to theta = 67.679 | 98.2 % |
| Absorption correction | Semi-empirical from equivalents |

| | |
|---|---|
| Max. and min. transmission | 1.00000 and 0.67877 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 2895 / 0 / 197 |
| Goodness-of-fit on F^2 | 1.068 |
| Final R indices [I>2sigma(I)] | R1 = 0.0358, wR2 = 0.0960 |
| R indices (all data) | R1 = 0.0360, wR2 = 0.0962 |
| Extinction coefficient | 0.0024(3) |

Table C.2j Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for yd1cl. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Cl(1) | 542(1) | 6842(1) | 6036(1) | 31(1) |
| O(1) | 3914(1) | 636(1) | 7036(1) | 20(1) |
| O(2) | 3718(1) | 5365(1) | 4686(1) | 19(1) |
| O(3) | 4779(1) | 5732(1) | 6109(1) | 21(1) |
| C(1) | 1522(1) | 5602(2) | 6246(1) | 23(1) |
| C(2) | 2282(1) | 6655(2) | 6413(1) | 24(1) |
| C(3) | 3065(1) | 5685(2) | 6579(1) | 21(1) |
| C(4) | 3094(1) | 3650(2) | 6576(1) | 18(1) |
| C(5) | 2319(1) | 2634(2) | 6414(1) | 20(1) |
| C(6) | 1527(1) | 3588(2) | 6244(1) | 22(1) |
| C(7) | 3952(1) | 2592(2) | 6742(1) | 17(1) |
| C(8) | 4146(1) | 2529(2) | 5819(1) | 17(1) |
| C(9) | 4230(1) | 4638(2) | 5542(1) | 17(1) |
| C(10) | 3061(1) | 4213(2) | 3901(1) | 19(1) |
| C(11) | 3314(1) | 2075(2) | 4023(1) | 20(1) |
| C(12) | 3427(1) | 1355(2) | 5010(1) | 19(1) |
| C(13) | 5058(1) | 1591(2) | 6074(1) | 21(1) |
| C(14) | 2144(1) | 4675(2) | 3845(1) | 20(1) |
| C(15) | 1940(1) | 6848(2) | 3787(1) | 22(1) |
| C(16) | 1000(1) | 7266(2) | 3672(1) | 24(1) |
| C(17) | 822(1) | 9437(2) | 3702(1) | 36(1) |

Table C.3j Bond lengths [A] and angles [deg] for yd1cl.

| | |
|---|---|
| Cl(1)-C(1) | 1.7428(13) |
| O(1)-C(7) | 1.4269(15) |
| O(1)-H(1) | 0.87(2) |
| O(2)-C(9) | 1.3240(15) |
| O(2)-C(10) | 1.4720(15) |

| | |
|---|---|
| O(3)-C(9) | 1.2204(16) |
| C(1)-C(2) | 1.382(2) |
| C(1)-C(6) | 1.384(2) |
| C(2)-C(3) | 1.3862(19) |
| C(2)-H(2) | 0.9500 |
| C(3)-C(4) | 1.4000(18) |
| C(3)-H(3) | 0.9500 |
| C(4)-C(5) | 1.3910(19) |
| C(4)-C(7) | 1.5211(17) |
| C(5)-C(6) | 1.3920(19) |
| C(5)-H(5) | 0.9500 |
| C(6)-H(6) | 0.9500 |
| C(7)-C(8) | 1.5656(17) |
| C(7)-H(7) | 1.0000 |
| C(8)-C(9) | 1.5318(16) |
| C(8)-C(13) | 1.5379(17) |
| C(8)-C(12) | 1.5409(17) |
| C(10)-C(14) | 1.5186(18) |
| C(10)-C(11) | 1.5187(18) |
| C(10)-H(10) | 1.0000 |
| C(11)-C(12) | 1.5176(18) |
| C(11)-H(11A) | 0.9900 |
| C(11)-H(11B) | 0.9900 |
| C(12)-H(12A) | 0.9900 |
| C(12)-H(12B) | 0.9900 |
| C(13)-H(13A) | 0.9800 |
| C(13)-H(13B) | 0.9800 |
| C(13)-H(13C) | 0.9800 |
| C(14)-C(15) | 1.5262(17) |
| C(14)-H(14A) | 0.9900 |
| C(14)-H(14B) | 0.9900 |
| C(15)-C(16) | 1.5214(19) |
| C(15)-H(15A) | 0.9900 |
| C(15)-H(15B) | 0.9900 |
| C(16)-C(17) | 1.525(2) |
| C(16)-H(16A) | 0.9900 |
| C(16)-H(16B) | 0.9900 |
| C(17)-H(17A) | 0.9800 |
| C(17)-H(17B) | 0.9800 |
| C(17)-H(17C) | 0.9800 |
| C(7)-O(1)-H(1) | 106.0(13) |
| C(9)-O(2)-C(10) | 123.62(10) |
| C(2)-C(1)-C(6) | 121.18(12) |
| C(2)-C(1)-Cl(1) | 119.14(10) |
| C(6)-C(1)-Cl(1) | 119.68(11) |
| C(1)-C(2)-C(3) | 119.67(12) |

| | |
|---|---|
| C(1)-C(2)-H(2) | 120.2 |
| C(3)-C(2)-H(2) | 120.2 |
| C(2)-C(3)-C(4) | 120.72(12) |
| C(2)-C(3)-H(3) | 119.6 |
| C(4)-C(3)-H(3) | 119.6 |
| C(5)-C(4)-C(3) | 118.13(12) |
| C(5)-C(4)-C(7) | 121.32(11) |
| C(3)-C(4)-C(7) | 120.55(11) |
| C(4)-C(5)-C(6) | 121.77(12) |
| C(4)-C(5)-H(5) | 119.1 |
| C(6)-C(5)-H(5) | 119.1 |
| C(1)-C(6)-C(5) | 118.52(13) |
| C(1)-C(6)-H(6) | 120.7 |
| C(5)-C(6)-H(6) | 120.7 |
| O(1)-C(7)-C(4) | 110.15(10) |
| O(1)-C(7)-C(8) | 107.87(10) |
| C(4)-C(7)-C(8) | 112.81(10) |
| O(1)-C(7)-H(7) | 108.6 |
| C(4)-C(7)-H(7) | 108.6 |
| C(8)-C(7)-H(7) | 108.6 |
| C(9)-C(8)-C(13) | 105.94(10) |
| C(9)-C(8)-C(12) | 113.85(10) |
| C(13)-C(8)-C(12) | 109.73(10) |
| C(9)-C(8)-C(7) | 107.20(10) |
| C(13)-C(8)-C(7) | 109.20(10) |
| C(12)-C(8)-C(7) | 110.72(10) |
| O(3)-C(9)-O(2) | 116.75(11) |
| O(3)-C(9)-C(8) | 121.00(11) |
| O(2)-C(9)-C(8) | 122.25(11) |
| O(2)-C(10)-C(14) | 108.75(10) |
| O(2)-C(10)-C(11) | 110.32(10) |
| C(14)-C(10)-C(11) | 115.40(11) |
| O(2)-C(10)-H(10) | 107.3 |
| C(14)-C(10)-H(10) | 107.3 |
| C(11)-C(10)-H(10) | 107.3 |
| C(12)-C(11)-C(10) | 110.56(10) |
| C(12)-C(11)-H(11A) | 109.5 |
| C(10)-C(11)-H(11A) | 109.5 |
| C(12)-C(11)-H(11B) | 109.5 |
| C(10)-C(11)-H(11B) | 109.5 |
| H(11A)-C(11)-H(11B) | 108.1 |
| C(11)-C(12)-C(8) | 111.00(10) |
| C(11)-C(12)-H(12A) | 109.4 |
| C(8)-C(12)-H(12A) | 109.4 |
| C(11)-C(12)-H(12B) | 109.4 |
| C(8)-C(12)-H(12B) | 109.4 |

| | |
|---|---|
| H(12A)-C(12)-H(12B) | 108.0 |
| C(8)-C(13)-H(13A) | 109.5 |
| C(8)-C(13)-H(13B) | 109.5 |
| H(13A)-C(13)-H(13B) | 109.5 |
| C(8)-C(13)-H(13C) | 109.5 |
| H(13A)-C(13)-H(13C) | 109.5 |
| H(13B)-C(13)-H(13C) | 109.5 |
| C(10)-C(14)-C(15) | 113.64(11) |
| C(10)-C(14)-H(14A) | 108.8 |
| C(15)-C(14)-H(14A) | 108.8 |
| C(10)-C(14)-H(14B) | 108.8 |
| C(15)-C(14)-H(14B) | 108.8 |
| H(14A)-C(14)-H(14B) | 107.7 |
| C(16)-C(15)-C(14) | 112.56(11) |
| C(16)-C(15)-H(15A) | 109.1 |
| C(14)-C(15)-H(15A) | 109.1 |
| C(16)-C(15)-H(15B) | 109.1 |
| C(14)-C(15)-H(15B) | 109.1 |
| H(15A)-C(15)-H(15B) | 107.8 |
| C(15)-C(16)-C(17) | 112.44(12) |
| C(15)-C(16)-H(16A) | 109.1 |
| C(17)-C(16)-H(16A) | 109.1 |
| C(15)-C(16)-H(16B) | 109.1 |
| C(17)-C(16)-H(16B) | 109.1 |
| H(16A)-C(16)-H(16B) | 107.8 |
| C(16)-C(17)-H(17A) | 109.5 |
| C(16)-C(17)-H(17B) | 109.5 |
| H(17A)-C(17)-H(17B) | 109.5 |
| C(16)-C(17)-H(17C) | 109.5 |
| H(17A)-C(17)-H(17C) | 109.5 |
| H(17B)-C(17)-H(17C) | 109.5 |

Table C.4j Anisotropic displacement parameters (A^2 x 10^3) for yd1cl. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Cl(1) | 29(1) | 30(1) | 34(1) | -1(1) | 14(1) | 11(1) |
| O(1) | 25(1) | 14(1) | 19(1) | 4(1) | 7(1) | 1(1) |
| O(2) | 21(1) | 15(1) | 18(1) | 1(1) | 6(1) | -1(1) |
| O(3) | 22(1) | 18(1) | 21(1) | -2(1) | 7(1) | -3(1) |
| C(1) | 26(1) | 23(1) | 20(1) | 0(1) | 10(1) | 7(1) |
| C(2) | 34(1) | 14(1) | 25(1) | -1(1) | 14(1) | 3(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(3) | 27(1) | 16(1) | 20(1) | -2(1) | 11(1) | -2(1) |
| C(4) | 24(1) | 16(1) | 13(1) | 0(1) | 7(1) | 1(1) |
| C(5) | 26(1) | 15(1) | 18(1) | 1(1) | 9(1) | 1(1) |
| C(6) | 23(1) | 22(1) | 20(1) | 0(1) | 9(1) | -1(1) |
| C(7) | 22(1) | 13(1) | 15(1) | 1(1) | 6(1) | -1(1) |
| C(8) | 21(1) | 13(1) | 16(1) | 0(1) | 7(1) | 1(1) |
| C(9) | 18(1) | 16(1) | 18(1) | 0(1) | 9(1) | 2(1) |
| C(10) | 22(1) | 19(1) | 14(1) | -1(1) | 5(1) | -1(1) |
| C(11) | 23(1) | 18(1) | 18(1) | -3(1) | 7(1) | 2(1) |
| C(12) | 22(1) | 14(1) | 18(1) | -2(1) | 6(1) | 0(1) |
| C(13) | 21(1) | 18(1) | 21(1) | 1(1) | 8(1) | 3(1) |
| C(14) | 22(1) | 18(1) | 19(1) | 0(1) | 6(1) | 0(1) |
| C(15) | 22(1) | 18(1) | 23(1) | 2(1) | 8(1) | 1(1) |
| C(16) | 25(1) | 22(1) | 24(1) | 1(1) | 8(1) | 3(1) |
| C(17) | 32(1) | 26(1) | 47(1) | -1(1) | 13(1) | 9(1) |

Table C.5j Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for yd1cl.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 4334(14) | 530(30) | 7613(16) | 42(5) |
| H(2) | 2267 | 8036 | 6415 | 29 |
| H(3) | 3588 | 6410 | 6697 | 25 |
| H(5) | 2331 | 1253 | 6419 | 24 |
| H(6) | 1003 | 2874 | 6129 | 26 |
| H(7) | 4453 | 3274 | 7267 | 21 |
| H(10) | 3078 | 4660 | 3284 | 23 |
| H(11A) | 2847 | 1305 | 3516 | 24 |
| H(11B) | 3875 | 1891 | 3948 | 24 |
| H(12A) | 3594 | -38 | 5077 | 22 |
| H(12B) | 2857 | 1477 | 5071 | 22 |
| H(13A) | 5048 | 243 | 6280 | 31 |
| H(13B) | 5511 | 2324 | 6600 | 31 |
| H(13C) | 5196 | 1610 | 5507 | 31 |
| H(14A) | 2091 | 4129 | 4420 | 24 |
| H(14B) | 1696 | 4027 | 3269 | 24 |
| H(15A) | 2363 | 7490 | 4382 | 26 |
| H(15B) | 2025 | 7414 | 3234 | 26 |
| H(16A) | 897 | 6603 | 4195 | 29 |
| H(16B) | 576 | 6725 | 3049 | 29 |
| H(17A) | 1215 | 9964 | 4333 | 54 |
| H(17B) | 204 | 9636 | 3598 | 54 |

| | | | | |
|---|---|---|---|---|
| H(17C) | 935 | 10104 | 3195 | 54 |

Table C.6j Torsion angles [deg] for yd1cl.

| | |
|---|---|
| C(6)-C(1)-C(2)-C(3) | 0.2(2) |
| Cl(1)-C(1)-C(2)-C(3) | -179.87(10) |
| C(1)-C(2)-C(3)-C(4) | 0.2(2) |
| C(2)-C(3)-C(4)-C(5) | -0.84(19) |
| C(2)-C(3)-C(4)-C(7) | 179.00(11) |
| C(3)-C(4)-C(5)-C(6) | 1.00(19) |
| C(7)-C(4)-C(5)-C(6) | -178.84(11) |
| C(2)-C(1)-C(6)-C(5) | -0.1(2) |
| Cl(1)-C(1)-C(6)-C(5) | -179.98(10) |
| C(4)-C(5)-C(6)-C(1) | -0.55(19) |
| C(5)-C(4)-C(7)-O(1) | -20.22(16) |
| C(3)-C(4)-C(7)-O(1) | 159.95(11) |
| C(5)-C(4)-C(7)-C(8) | 100.38(13) |
| C(3)-C(4)-C(7)-C(8) | -79.45(14) |
| O(1)-C(7)-C(8)-C(9) | -177.18(9) |
| C(4)-C(7)-C(8)-C(9) | 60.93(13) |
| O(1)-C(7)-C(8)-C(13) | -62.84(12) |
| C(4)-C(7)-C(8)-C(13) | 175.27(10) |
| O(1)-C(7)-C(8)-C(12) | 58.09(13) |
| C(4)-C(7)-C(8)-C(12) | -63.80(13) |
| C(10)-O(2)-C(9)-O(3) | 176.20(10) |
| C(10)-O(2)-C(9)-C(8) | -3.73(17) |
| C(13)-C(8)-C(9)-O(3) | -58.50(14) |
| C(12)-C(8)-C(9)-O(3) | -179.17(11) |
| C(7)-C(8)-C(9)-O(3) | 58.02(15) |
| C(13)-C(8)-C(9)-O(2) | 121.43(12) |
| C(12)-C(8)-C(9)-O(2) | 0.75(16) |
| C(7)-C(8)-C(9)-O(2) | -122.05(12) |
| C(9)-O(2)-C(10)-C(14) | 102.92(13) |
| C(9)-O(2)-C(10)-C(11) | -24.58(15) |
| O(2)-C(10)-C(11)-C(12) | 55.53(13) |
| C(14)-C(10)-C(11)-C(12) | -68.20(14) |
| C(10)-C(11)-C(12)-C(8) | -58.87(13) |
| C(9)-C(8)-C(12)-C(11) | 30.28(14) |
| C(13)-C(8)-C(12)-C(11) | -88.25(12) |
| C(7)-C(8)-C(12)-C(11) | 151.14(10) |
| O(2)-C(10)-C(14)-C(15) | 51.76(14) |
| C(11)-C(10)-C(14)-C(15) | 176.31(11) |
| C(10)-C(14)-C(15)-C(16) | 176.64(11) |
| C(14)-C(15)-C(16)-C(17) | 175.07(12) |

Table C.7j Hydrogen bonds for yd1cl [A and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(1)-H(1)...O(3)#1 | 0.87(2) | 1.90(2) | 2.7590(13) | 170.8(19) |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y-1/2,-z+3/2

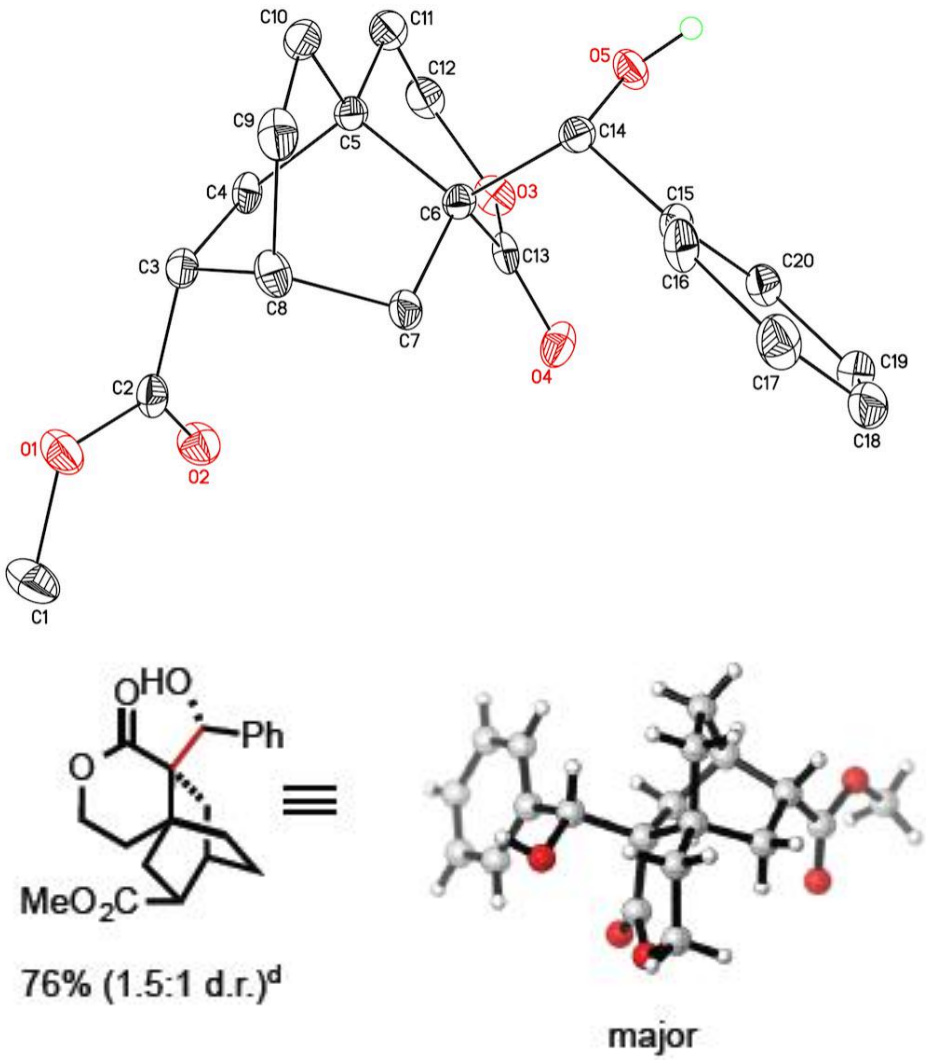



Figure C.11 Structure of yddaph.

**Structure Determination.**

Colorless needles of **yddaph** were grown from a dichloromethane/hexanes solution of the compound at 22 deg. C. A crystal of dimensions 0.22 x 0.03 x 0.03 mm was mounted on a

Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (ë = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ù. The exposure times were 1 sec. for the low angle images, 5 sec. for high angle. The integration of the data yielded a total of 13141 reflections to a maximum 2è value of 136.31° of which 2822 were independent and 2659 were greater than 2ó(I). The final cell constants (Table 1) were based on the xyz centroids 8706 reflections above 10ó(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group P2(1) with Z = 2 for the formula $C_{20}H_{24}O_5$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in both idealized and refined positions. Full matrix least-squares refinement based on $F^2$ converged at R1 = 0.0392 and wR2 = 0.1007 [based on I > 2sigma(I)], R1 = 0.0417 and wR2 = 0.1029 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.
Sheldrick, G.M. SHELXTL, v. 2014/6; Bruker Analytical X-ray, Madison, WI, 2014.
CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

Table C.1k Crystal data and structure refinement for yddaph.

| | |
|---|---|
| Identification code | yddaph |
| Empirical formula | C20 H24 O5 |
| Formula weight | 344.39 |
| Temperature | 85(2) K |
| Wavelength | 1.54178 A |
| Crystal system, space group | Monoclinic, P2(1) |
| Unit cell dimensions | a = 9.5391(2) A alpha = 90 deg.<br>b = 7.04260(10) A beta = 98.518(7) deg.<br>c = 12.7096(9) A gamma = 90 deg. |
| Volume | 844.41(7) A^3 |
| Z, Calculated density | 2, 1.354 Mg/m^3 |
| Absorption coefficient | 0.790 mm^-1 |
| F(000) | 368 |
| Crystal size | 0.220 x 0.030 x 0.030 mm |
| Theta range for data collection | 3.516 to 68.153 deg. |
| Limiting indices | -11<=h<=11, -8<=k<=8, -15<=l<=15 |
| Reflections collected / unique | 13141 / 2822 [R(int) = 0.0604] |
| Completeness to theta = 67.679 | 100.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.977 and 0.780 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 2822 / 1 / 232 |
| Goodness-of-fit on F^2 | 1.093 |

Final R indices [I>2sigma(I)] R1 = 0.0392, wR2 = 0.1007
R indices (all data) R1 = 0.0417, wR2 = 0.1029
Absolute structure parameter -0.10(17)
Extinction coefficient 0.0074(16)
Largest diff. peak and hole 0.185 and -0.175 e.A^-3

Table C.2k Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for yddaph. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 1518(2) | 5015(3) | 10174(2) | 24(1) |
| O(2) | 2332(2) | 7630(3) | 9454(2) | 24(1) |
| O(3) | 5306(2) | 8187(3) | 6877(2) | 21(1) |
| O(4) | 3064(2) | 8244(3) | 6249(2) | 24(1) |
| O(5) | 5196(2) | 5021(3) | 5412(2) | 20(1) |
| C(1) | 412(3) | 6154(5) | 10529(3) | 29(1) |
| C(2) | 2399(3) | 5940(5) | 9617(2) | 18(1) |
| C(3) | 3396(3) | 4554(4) | 9216(2) | 17(1) |
| C(4) | 4710(3) | 5507(4) | 8865(2) | 17(1) |
| C(5) | 5081(3) | 4577(4) | 7835(2) | 16(1) |
| C(6) | 3911(3) | 5199(4) | 6905(2) | 14(1) |
| C(7) | 2455(3) | 4809(4) | 7281(2) | 17(1) |
| C(8) | 2620(3) | 3472(4) | 8238(2) | 18(1) |
| C(9) | 3518(3) | 1752(4) | 8025(2) | 21(1) |
| C(10) | 5050(3) | 2418(5) | 7994(2) | 20(1) |
| C(11) | 6532(3) | 5248(5) | 7633(2) | 21(1) |
| C(12) | 6567(3) | 7386(5) | 7508(2) | 24(1) |
| C(13) | 4049(3) | 7294(4) | 6675(2) | 17(1) |
| C(14) | 4023(3) | 4175(4) | 5816(2) | 16(1) |
| C(15) | 2685(3) | 4268(4) | 4996(2) | 16(1) |
| C(16) | 1749(3) | 2740(5) | 4895(2) | 20(1) |
| C(17) | 489(3) | 2815(5) | 4178(2) | 24(1) |
| C(18) | 196(3) | 4398(5) | 3536(2) | 25(1) |
| C(19) | 1145(3) | 5897(5) | 3605(2) | 23(1) |
| C(20) | 2394(3) | 5837(4) | 4332(2) | 19(1) |

Table C.3k Bond lengths [A] and angles [deg] for yddaph.

| | |
|---|---|
| O(1)-C(2) | 1.345(4) |
| O(1)-C(1) | 1.449(4) |
| O(2)-C(2) | 1.207(4) |

| | |
|---|---|
| O(3)-C(13) | 1.344(4) |
| O(3)-C(12) | 1.457(4) |
| O(4)-C(13) | 1.214(4) |
| O(5)-C(14) | 1.428(3) |
| O(5)-H(5) | 0.88(6) |
| C(1)-H(1A) | 0.9800 |
| C(1)-H(1B) | 0.9800 |
| C(1)-H(1C) | 0.9800 |
| C(2)-C(3) | 1.504(4) |
| C(3)-C(4) | 1.544(4) |
| C(3)-C(8) | 1.550(4) |
| C(3)-H(3) | 1.0000 |
| C(4)-C(5) | 1.550(4) |
| C(4)-H(4A) | 0.9900 |
| C(4)-H(4B) | 0.9900 |
| C(5)-C(11) | 1.521(4) |
| C(5)-C(10) | 1.534(4) |
| C(5)-C(6) | 1.563(4) |
| C(6)-C(13) | 1.514(4) |
| C(6)-C(7) | 1.558(4) |
| C(6)-C(14) | 1.578(4) |
| C(7)-C(8) | 1.528(4) |
| C(7)-H(7A) | 0.9900 |
| C(7)-H(7B) | 0.9900 |
| C(8)-C(9) | 1.531(4) |
| C(8)-H(8) | 1.0000 |
| C(9)-C(10) | 1.541(4) |
| C(9)-H(9A) | 0.9900 |
| C(9)-H(9B) | 0.9900 |
| C(10)-H(10A) | 0.9900 |
| C(10)-H(10B) | 0.9900 |
| C(11)-C(12) | 1.515(5) |
| C(11)-H(11A) | 0.9900 |
| C(11)-H(11B) | 0.9900 |
| C(12)-H(12A) | 0.9900 |
| C(12)-H(12B) | 0.9900 |
| C(14)-C(15) | 1.525(4) |
| C(14)-H(14) | 1.0000 |
| C(15)-C(16) | 1.392(4) |
| C(15)-C(20) | 1.393(4) |
| C(16)-C(17) | 1.398(4) |
| C(16)-H(16) | 0.9500 |
| C(17)-C(18) | 1.386(5) |
| C(17)-H(17) | 0.9500 |
| C(18)-C(19) | 1.385(5) |
| C(18)-H(18) | 0.9500 |

| | |
|---|---|
| C(19)-C(20) | 1.396(4) |
| C(19)-H(19) | 0.9500 |
| C(20)-H(20) | 0.9500 |
| C(2)-O(1)-C(1) | 115.8(3) |
| C(13)-O(3)-C(12) | 124.3(2) |
| C(14)-O(5)-H(5) | 99(4) |
| O(1)-C(1)-H(1A) | 109.5 |
| O(1)-C(1)-H(1B) | 109.5 |
| H(1A)-C(1)-H(1B) | 109.5 |
| O(1)-C(1)-H(1C) | 109.5 |
| H(1A)-C(1)-H(1C) | 109.5 |
| H(1B)-C(1)-H(1C) | 109.5 |
| O(2)-C(2)-O(1) | 123.1(3) |
| O(2)-C(2)-C(3) | 127.0(3) |
| O(1)-C(2)-C(3) | 109.9(3) |
| C(2)-C(3)-C(4) | 113.4(2) |
| C(2)-C(3)-C(8) | 109.9(2) |
| C(4)-C(3)-C(8) | 107.1(2) |
| C(2)-C(3)-H(3) | 108.8 |
| C(4)-C(3)-H(3) | 108.8 |
| C(8)-C(3)-H(3) | 108.8 |
| C(3)-C(4)-C(5) | 110.9(2) |
| C(3)-C(4)-H(4A) | 109.5 |
| C(5)-C(4)-H(4A) | 109.5 |
| C(3)-C(4)-H(4B) | 109.5 |
| C(5)-C(4)-H(4B) | 109.5 |
| H(4A)-C(4)-H(4B) | 108.1 |
| C(11)-C(5)-C(10) | 111.5(2) |
| C(11)-C(5)-C(4) | 109.8(2) |
| C(10)-C(5)-C(4) | 107.2(2) |
| C(11)-C(5)-C(6) | 110.5(2) |
| C(10)-C(5)-C(6) | 110.6(2) |
| C(4)-C(5)-C(6) | 107.1(2) |
| C(13)-C(6)-C(7) | 109.8(2) |
| C(13)-C(6)-C(5) | 110.3(2) |
| C(7)-C(6)-C(5) | 106.7(2) |
| C(13)-C(6)-C(14) | 104.9(2) |
| C(7)-C(6)-C(14) | 111.5(2) |
| C(5)-C(6)-C(14) | 113.7(2) |
| C(8)-C(7)-C(6) | 111.2(2) |
| C(8)-C(7)-H(7A) | 109.4 |
| C(6)-C(7)-H(7A) | 109.4 |
| C(8)-C(7)-H(7B) | 109.4 |
| C(6)-C(7)-H(7B) | 109.4 |
| H(7A)-C(7)-H(7B) | 108.0 |
| C(7)-C(8)-C(9) | 110.0(2) |

| | |
|---|---|
| C(7)-C(8)-C(3) | 108.5(2) |
| C(9)-C(8)-C(3) | 108.5(2) |
| C(7)-C(8)-H(8) | 110.0 |
| C(9)-C(8)-H(8) | 110.0 |
| C(3)-C(8)-H(8) | 110.0 |
| C(8)-C(9)-C(10) | 108.7(3) |
| C(8)-C(9)-H(9A) | 109.9 |
| C(10)-C(9)-H(9A) | 109.9 |
| C(8)-C(9)-H(9B) | 109.9 |
| C(10)-C(9)-H(9B) | 109.9 |
| H(9A)-C(9)-H(9B) | 108.3 |
| C(5)-C(10)-C(9) | 110.0(2) |
| C(5)-C(10)-H(10A) | 109.7 |
| C(9)-C(10)-H(10A) | 109.7 |
| C(5)-C(10)-H(10B) | 109.7 |
| C(9)-C(10)-H(10B) | 109.7 |
| H(10A)-C(10)-H(10B) | 108.2 |
| C(12)-C(11)-C(5) | 111.2(3) |
| C(12)-C(11)-H(11A) | 109.4 |
| C(5)-C(11)-H(11A) | 109.4 |
| C(12)-C(11)-H(11B) | 109.4 |
| C(5)-C(11)-H(11B) | 109.4 |
| H(11A)-C(11)-H(11B) | 108.0 |
| O(3)-C(12)-C(11) | 114.4(3) |
| O(3)-C(12)-H(12A) | 108.7 |
| C(11)-C(12)-H(12A) | 108.7 |
| O(3)-C(12)-H(12B) | 108.7 |
| C(11)-C(12)-H(12B) | 108.7 |
| H(12A)-C(12)-H(12B) | 107.6 |
| O(4)-C(13)-O(3) | 116.0(3) |
| O(4)-C(13)-C(6) | 122.6(3) |
| O(3)-C(13)-C(6) | 121.3(3) |
| O(5)-C(14)-C(15) | 110.9(2) |
| O(5)-C(14)-C(6) | 106.5(2) |
| C(15)-C(14)-C(6) | 114.9(2) |
| O(5)-C(14)-H(14) | 108.1 |
| C(15)-C(14)-H(14) | 108.1 |
| C(6)-C(14)-H(14) | 108.1 |
| C(16)-C(15)-C(20) | 119.3(3) |
| C(16)-C(15)-C(14) | 119.3(3) |
| C(20)-C(15)-C(14) | 121.3(3) |
| C(15)-C(16)-C(17) | 120.6(3) |
| C(15)-C(16)-H(16) | 119.7 |
| C(17)-C(16)-H(16) | 119.7 |
| C(18)-C(17)-C(16) | 119.6(3) |
| C(18)-C(17)-H(17) | 120.2 |

| | |
|---|---|
| C(16)-C(17)-H(17) | 120.2 |
| C(19)-C(18)-C(17) | 120.2(3) |
| C(19)-C(18)-H(18) | 119.9 |
| C(17)-C(18)-H(18) | 119.9 |
| C(18)-C(19)-C(20) | 120.3(3) |
| C(18)-C(19)-H(19) | 119.8 |
| C(20)-C(19)-H(19) | 119.8 |
| C(15)-C(20)-C(19) | 119.9(3) |
| C(15)-C(20)-H(20) | 120.0 |
| C(19)-C(20)-H(20) | 120.0 |

Table C.4k Anisotropic displacement parameters (A^2 x 10^3) for yddaph. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| O(1) | 27(1) | 22(1) | 25(1) | 2(1) | 13(1) | 0(1) |
| O(2) | 29(1) | 19(1) | 26(1) | -1(1) | 8(1) | 2(1) |
| O(3) | 23(1) | 18(1) | 25(1) | -2(1) | 7(1) | -4(1) |
| O(4) | 34(1) | 18(1) | 17(1) | 1(1) | -3(1) | 5(1) |
| O(5) | 16(1) | 29(1) | 15(1) | -3(1) | 6(1) | -1(1) |
| C(1) | 30(2) | 27(2) | 35(2) | -4(2) | 17(1) | 3(1) |
| C(2) | 20(1) | 22(2) | 12(1) | 1(1) | 1(1) | -3(1) |
| C(3) | 20(1) | 16(2) | 13(1) | 1(1) | 2(1) | 1(1) |
| C(4) | 21(1) | 18(2) | 10(1) | -1(1) | -1(1) | -2(1) |
| C(5) | 16(1) | 19(2) | 12(1) | -3(1) | -1(1) | 3(1) |
| C(6) | 14(1) | 15(2) | 13(1) | -2(1) | 0(1) | 0(1) |
| C(7) | 17(1) | 22(2) | 11(1) | -2(1) | 1(1) | 0(1) |
| C(8) | 24(1) | 17(2) | 15(1) | -3(1) | 5(1) | -4(1) |
| C(9) | 35(2) | 12(1) | 17(1) | 0(1) | 5(1) | -1(1) |
| C(10) | 25(2) | 18(2) | 15(1) | 0(1) | 0(1) | 5(1) |
| C(11) | 16(1) | 28(2) | 18(1) | -3(1) | 0(1) | -2(1) |
| C(12) | 17(1) | 33(2) | 20(1) | -4(1) | 3(1) | -6(1) |
| C(13) | 24(2) | 18(2) | 9(1) | -1(1) | 4(1) | -2(1) |
| C(14) | 16(1) | 16(1) | 15(1) | -2(1) | 1(1) | 1(1) |
| C(15) | 17(1) | 20(2) | 12(1) | -3(1) | 0(1) | -1(1) |
| C(16) | 24(1) | 24(2) | 12(1) | -2(1) | 2(1) | -4(1) |
| C(17) | 21(1) | 32(2) | 18(1) | -5(1) | 2(1) | -8(1) |
| C(18) | 18(1) | 41(2) | 16(1) | -6(1) | 1(1) | 1(1) |
| C(19) | 22(1) | 30(2) | 16(1) | -1(1) | 1(1) | 5(1) |
| C(20) | 22(1) | 21(2) | 14(1) | -2(1) | 3(1) | 1(1) |

Table C.5k Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for yddaph.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(5) | 5220(60) | 4290(80) | 4850(50) | 62(15) |
| H(1A) | 843 | 7166 | 10998 | 44 |
| H(1B) | -176 | 5349 | 10916 | 44 |
| H(1C) | -178 | 6717 | 9910 | 44 |
| H(3) | 3720 | 3617 | 9792 | 20 |
| H(4A) | 5527 | 5385 | 9440 | 20 |
| H(4B) | 4519 | 6876 | 8738 | 20 |
| H(7A) | 2039 | 6024 | 7475 | 20 |
| H(7B) | 1798 | 4236 | 6690 | 20 |
| H(8) | 1666 | 3045 | 8381 | 22 |
| H(9A) | 3126 | 1160 | 7338 | 26 |
| H(9B) | 3504 | 796 | 8595 | 26 |
| H(10A) | 5655 | 2074 | 8668 | 23 |
| H(10B) | 5431 | 1776 | 7404 | 23 |
| H(11A) | 7256 | 4860 | 8235 | 25 |
| H(11B) | 6768 | 4638 | 6980 | 25 |
| H(12A) | 6689 | 7973 | 8224 | 28 |
| H(12B) | 7404 | 7730 | 7171 | 28 |
| H(14) | 4252 | 2808 | 5969 | 19 |
| H(16) | 1969 | 1637 | 5318 | 24 |
| H(17) | -162 | 1787 | 4131 | 28 |
| H(18) | -659 | 4456 | 3047 | 30 |
| H(19) | 946 | 6971 | 3155 | 27 |
| H(20) | 3044 | 6865 | 4374 | 23 |

Table C.6k Torsion angles [deg] for yddaph.

| | |
|---|---|
| C(1)-O(1)-C(2)-O(2) | 3.3(4) |
| C(1)-O(1)-C(2)-C(3) | -174.6(2) |
| O(2)-C(2)-C(3)-C(4) | 19.4(4) |
| O(1)-C(2)-C(3)-C(4) | -162.8(2) |
| O(2)-C(2)-C(3)-C(8) | -100.4(3) |
| O(1)-C(2)-C(3)-C(8) | 77.4(3) |
| C(2)-C(3)-C(4)-C(5) | -139.7(2) |
| C(8)-C(3)-C(4)-C(5) | -18.3(3) |
| C(3)-C(4)-C(5)-C(11) | -168.4(2) |
| C(3)-C(4)-C(5)-C(10) | -47.2(3) |

| | |
|---|---|
| C(3)-C(4)-C(5)-C(6) | 71.5(3) |
| C(11)-C(5)-C(6)-C(13) | -50.0(3) |
| C(10)-C(5)-C(6)-C(13) | -173.9(2) |
| C(4)-C(5)-C(6)-C(13) | 69.6(3) |
| C(11)-C(5)-C(6)-C(7) | -169.2(2) |
| C(10)-C(5)-C(6)-C(7) | 66.9(3) |
| C(4)-C(5)-C(6)-C(7) | -49.6(3) |
| C(11)-C(5)-C(6)-C(14) | 67.4(3) |
| C(10)-C(5)-C(6)-C(14) | -56.5(3) |
| C(4)-C(5)-C(6)-C(14) | -173.0(2) |
| C(13)-C(6)-C(7)-C(8) | -136.0(2) |
| C(5)-C(6)-C(7)-C(8) | -16.5(3) |
| C(14)-C(6)-C(7)-C(8) | 108.3(3) |
| C(6)-C(7)-C(8)-C(9) | -48.1(3) |
| C(6)-C(7)-C(8)-C(3) | 70.4(3) |
| C(2)-C(3)-C(8)-C(7) | 74.8(3) |
| C(4)-C(3)-C(8)-C(7) | -48.7(3) |
| C(2)-C(3)-C(8)-C(9) | -165.8(2) |
| C(4)-C(3)-C(8)-C(9) | 70.7(3) |
| C(7)-C(8)-C(9)-C(10) | 68.1(3) |
| C(3)-C(8)-C(9)-C(10) | -50.3(3) |
| C(11)-C(5)-C(10)-C(9) | -171.4(2) |
| C(4)-C(5)-C(10)-C(9) | 68.4(3) |
| C(6)-C(5)-C(10)-C(9) | -48.0(3) |
| C(8)-C(9)-C(10)-C(5) | -17.5(3) |
| C(10)-C(5)-C(11)-C(12) | -178.4(2) |
| C(4)-C(5)-C(11)-C(12) | -59.7(3) |
| C(6)-C(5)-C(11)-C(12) | 58.2(3) |
| C(13)-O(3)-C(12)-C(11) | 19.0(4) |
| C(5)-C(11)-C(12)-O(3) | -41.7(3) |
| C(12)-O(3)-C(13)-O(4) | 171.2(2) |
| C(12)-O(3)-C(13)-C(6) | -12.6(4) |
| C(7)-C(6)-C(13)-O(4) | -39.0(3) |
| C(5)-C(6)-C(13)-O(4) | -156.3(2) |
| C(14)-C(6)-C(13)-O(4) | 80.9(3) |
| C(7)-C(6)-C(13)-O(3) | 145.0(2) |
| C(5)-C(6)-C(13)-O(3) | 27.7(3) |
| C(14)-C(6)-C(13)-O(3) | -95.1(3) |
| C(13)-C(6)-C(14)-O(5) | 46.0(3) |
| C(7)-C(6)-C(14)-O(5) | 164.7(2) |
| C(5)-C(6)-C(14)-O(5) | -74.5(3) |
| C(13)-C(6)-C(14)-C(15) | -77.2(3) |
| C(7)-C(6)-C(14)-C(15) | 41.5(3) |
| C(5)-C(6)-C(14)-C(15) | 162.3(2) |
| O(5)-C(14)-C(15)-C(16) | 141.8(3) |
| C(6)-C(14)-C(15)-C(16) | -97.4(3) |

| | |
|---|---|
| O(5)-C(14)-C(15)-C(20) | -37.0(4) |
| C(6)-C(14)-C(15)-C(20) | 83.8(3) |
| C(20)-C(15)-C(16)-C(17) | -3.5(4) |
| C(14)-C(15)-C(16)-C(17) | 177.6(3) |
| C(15)-C(16)-C(17)-C(18) | 2.3(4) |
| C(16)-C(17)-C(18)-C(19) | 0.0(5) |
| C(17)-C(18)-C(19)-C(20) | -0.9(4) |
| C(16)-C(15)-C(20)-C(19) | 2.6(4) |
| C(14)-C(15)-C(20)-C(19) | -178.6(3) |
| C(18)-C(19)-C(20)-C(15) | -0.3(4) |

Table C.7k Hydrogen bonds for yddaph [A and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(5)-H(5)...O(3)#1 | 0.88(6) | 2.31(6) | 3.153(3) | 159(5) |
| O(5)-H(5)...O(4)#1 | 0.88(6) | 2.42(6) | 3.134(3) | 138(5) |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y-1/2,-z+1

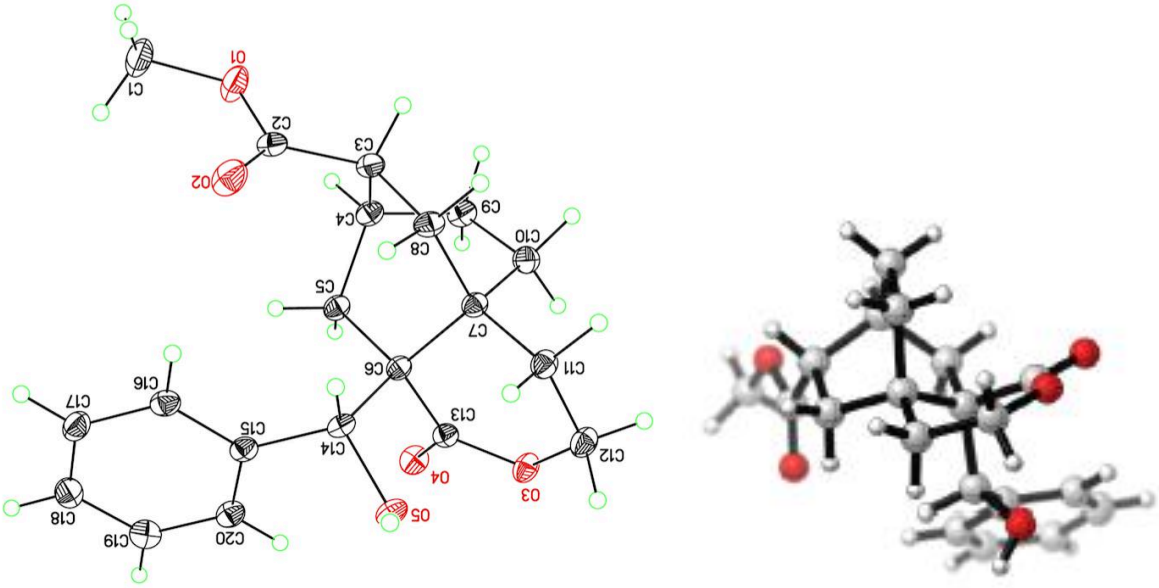



Figure C.12 Structure of sb353us.

**Structure Determination.**

Colorless plates of **sb353us** were grown from an ethyl acetate/hexane solution of the compound at 22 deg. C. A crystal of dimensions 0.26 x 0.26 x 0.12 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (ë = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected

with an oscillation width of 1.0° in ù. The exposure times were 1 sec. for the low angle images, 6 sec. for high angle. The integration of the data yielded a total of 25846 reflections to a maximum 2è value of 136.48° of which 3126 were independent and 3055 were greater than 2ó(I). The final cell constants (Table 1) were based on the xyz centroids 16650 reflections above 10ó(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group P2(1)/c with Z = 4 for the formula $C_{20}H_{25}O_5$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in both idealized and refined positions. Full matrix least-squares refinement based on $F^2$ converged at R1 = 0.0420 and wR2 = 0.0988 [based on I > 2sigma(I)], R1 = 0.0426 and wR2 = 0.0993 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.
Sheldrick, G.M. SHELXTL, v. 2014/6; Bruker Analytical X-ray, Madison, WI, 2014.
CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

Table C.1l Crystal data and structure refinement for sb353us.

| | |
|---|---|
| Identification code | sb353us |
| Empirical formula | C20 H24 O5 |
| Formula weight | 344.39 |
| Temperature | 85(2) K |
| Wavelength | 1.54178 A |
| Crystal system, space group | Monoclinic, P2(1)/c |
| Unit cell dimensions | a = 12.0682(9) A alpha = 90 deg.<br>b = 13.0615(2) A beta = 116.041(8) deg.<br>c = 12.0302(2) A gamma = 90 deg. |
| Volume | 1703.79(17) A^3 |
| Z, Calculated density | 4, 1.343 Mg/m^3 |
| Absorption coefficient | 0.783 mm^-1 |
| F(000) | 736 |
| Crystal size | 0.260 x 0.260 x 0.120 mm |
| Theta range for data collection | 4.077 to 68.238 deg. |
| Limiting indices | -14<=h<=14, -15<=k<=15, -14<=l<=14 |
| Reflections collected / unique | 25846 / 3126 [R(int) = 0.0611] |
| Completeness to theta = 67.679 | 100.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.000 and 0.816 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 3126 / 0 / 232 |
| Goodness-of-fit on F^2 | 1.108 |
| Final R indices [I>2sigma(I)] | R1 = 0.0420, wR2 = 0.0988 |
| R indices (all data) | R1 = 0.0426, wR2 = 0.0993 |
| Extinction coefficient | 0.0218(10) |
| Largest diff. peak and hole | 0.245 and -0.333 e.A^-3 |

Table C.2l Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for sb353us. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 6289(1) | 1730(1) | 4594(1) | 25(1) |
| O(2) | 4968(1) | 2394(1) | 5248(1) | 26(1) |
| O(3) | -188(1) | 1190(1) | 688(1) | 17(1) |
| O(4) | 731(1) | 2173(1) | -110(1) | 18(1) |
| O(5) | 289(1) | 2800(1) | 2397(1) | 16(1) |
| C(1) | 7189(1) | 2493(1) | 5302(1) | 28(1) |
| C(2) | 5199(1) | 1774(1) | 4637(1) | 16(1) |
| C(3) | 4345(1) | 944(1) | 3829(1) | 16(1) |
| C(4) | 3980(1) | 1126(1) | 2438(1) | 16(1) |
| C(5) | 3102(1) | 2037(1) | 1967(1) | 15(1) |
| C(6) | 1882(1) | 1840(1) | 2080(1) | 13(1) |
| C(7) | 2021(1) | 799(1) | 2771(1) | 14(1) |
| C(8) | 3167(1) | 828(1) | 4024(1) | 16(1) |
| C(9) | 3340(1) | 158(1) | 1742(1) | 19(1) |
| C(10) | 2229(1) | -76(1) | 2012(1) | 17(1) |
| C(11) | 854(1) | 588(1) | 2921(1) | 16(1) |
| C(12) | -281(1) | 592(1) | 1674(1) | 18(1) |
| C(13) | 780(1) | 1751(1) | 812(1) | 14(1) |
| C(14) | 1592(1) | 2759(1) | 2764(1) | 13(1) |
| C(15) | 2033(1) | 3800(1) | 2566(1) | 14(1) |
| C(16) | 3053(1) | 4249(1) | 3529(1) | 17(1) |
| C(17) | 3453(1) | 5220(1) | 3398(1) | 19(1) |
| C(18) | 2836(1) | 5753(1) | 2298(1) | 20(1) |
| C(19) | 1833(1) | 5305(1) | 1328(1) | 20(1) |
| C(20) | 1430(1) | 4336(1) | 1458(1) | 17(1) |

Table C.3l Bond lengths [A] and angles [deg] for sb353us.

| | |
|---|---|
| O(1)-C(2) | 1.3404(15) |
| O(1)-C(1) | 1.4448(16) |
| O(2)-C(2) | 1.2052(16) |
| O(3)-C(13) | 1.3309(15) |
| O(3)-C(12) | 1.4646(14) |
| O(4)-C(13) | 1.2163(15) |
| O(5)-C(14) | 1.4353(14) |
| O(5)-H(5) | 0.87(2) |
| C(1)-H(1A) | 0.9800 |

| | |
|---|---|
| C(1)-H(1B) | 0.9800 |
| C(1)-H(1C) | 0.9800 |
| C(2)-C(3) | 1.5167(17) |
| C(3)-C(8) | 1.5466(16) |
| C(3)-C(4) | 1.5503(16) |
| C(3)-H(3) | 1.0000 |
| C(4)-C(9) | 1.5259(17) |
| C(4)-C(5) | 1.5275(17) |
| C(4)-H(4) | 1.0000 |
| C(5)-C(6) | 1.5584(16) |
| C(5)-H(5A) | 0.9900 |
| C(5)-H(5B) | 0.9900 |
| C(6)-C(13) | 1.5264(15) |
| C(6)-C(7) | 1.5643(16) |
| C(6)-C(14) | 1.5780(16) |
| C(7)-C(11) | 1.5215(16) |
| C(7)-C(8) | 1.5351(16) |
| C(7)-C(10) | 1.5501(16) |
| C(8)-H(8A) | 0.9900 |
| C(8)-H(8B) | 0.9900 |
| C(9)-C(10) | 1.5421(17) |
| C(9)-H(9A) | 0.9900 |
| C(9)-H(9B) | 0.9900 |
| C(10)-H(10A) | 0.9900 |
| C(10)-H(10B) | 0.9900 |
| C(11)-C(12) | 1.5248(16) |
| C(11)-H(11A) | 0.9900 |
| C(11)-H(11B) | 0.9900 |
| C(12)-H(12A) | 0.9900 |
| C(12)-H(12B) | 0.9900 |
| C(14)-C(15) | 1.5165(17) |
| C(14)-H(14) | 1.0000 |
| C(15)-C(20) | 1.3949(17) |
| C(15)-C(16) | 1.3965(17) |
| C(16)-C(17) | 1.3906(18) |
| C(16)-H(16) | 0.9500 |
| C(17)-C(18) | 1.3869(19) |
| C(17)-H(17) | 0.9500 |
| C(18)-C(19) | 1.3892(19) |
| C(18)-H(18) | 0.9500 |
| C(19)-C(20) | 1.3891(18) |
| C(19)-H(19) | 0.9500 |
| C(20)-H(20) | 0.9500 |
| C(2)-O(1)-C(1) | 116.42(10) |
| C(13)-O(3)-C(12) | 125.38(9) |
| C(14)-O(5)-H(5) | 106.7(13) |

| | |
|---|---|
| O(1)-C(1)-H(1A) | 109.5 |
| O(1)-C(1)-H(1B) | 109.5 |
| H(1A)-C(1)-H(1B) | 109.5 |
| O(1)-C(1)-H(1C) | 109.5 |
| H(1A)-C(1)-H(1C) | 109.5 |
| H(1B)-C(1)-H(1C) | 109.5 |
| O(2)-C(2)-O(1) | 123.01(11) |
| O(2)-C(2)-C(3) | 126.70(11) |
| O(1)-C(2)-C(3) | 110.28(10) |
| C(2)-C(3)-C(8) | 112.56(10) |
| C(2)-C(3)-C(4) | 111.97(10) |
| C(8)-C(3)-C(4) | 109.53(9) |
| C(2)-C(3)-H(3) | 107.5 |
| C(8)-C(3)-H(3) | 107.5 |
| C(4)-C(3)-H(3) | 107.5 |
| C(9)-C(4)-C(5) | 109.90(10) |
| C(9)-C(4)-C(3) | 107.53(10) |
| C(5)-C(4)-C(3) | 109.95(10) |
| C(9)-C(4)-H(4) | 109.8 |
| C(5)-C(4)-H(4) | 109.8 |
| C(3)-C(4)-H(4) | 109.8 |
| C(4)-C(5)-C(6) | 111.57(10) |
| C(4)-C(5)-H(5A) | 109.3 |
| C(6)-C(5)-H(5A) | 109.3 |
| C(4)-C(5)-H(5B) | 109.3 |
| C(6)-C(5)-H(5B) | 109.3 |
| H(5A)-C(5)-H(5B) | 108.0 |
| C(13)-C(6)-C(5) | 111.56(9) |
| C(13)-C(6)-C(7) | 107.93(9) |
| C(5)-C(6)-C(7) | 107.72(9) |
| C(13)-C(6)-C(14) | 106.51(9) |
| C(5)-C(6)-C(14) | 110.73(9) |
| C(7)-C(6)-C(14) | 112.41(9) |
| C(11)-C(7)-C(8) | 111.70(9) |
| C(11)-C(7)-C(10) | 109.54(10) |
| C(8)-C(7)-C(10) | 106.70(9) |
| C(11)-C(7)-C(6) | 109.33(9) |
| C(8)-C(7)-C(6) | 109.91(9) |
| C(10)-C(7)-C(6) | 109.61(9) |
| C(7)-C(8)-C(3) | 110.20(9) |
| C(7)-C(8)-H(8A) | 109.6 |
| C(3)-C(8)-H(8A) | 109.6 |
| C(7)-C(8)-H(8B) | 109.6 |
| C(3)-C(8)-H(8B) | 109.6 |
| H(8A)-C(8)-H(8B) | 108.1 |
| C(4)-C(9)-C(10) | 109.02(10) |

| | |
|---|---|
| C(4)-C(9)-H(9A) | 109.9 |
| C(10)-C(9)-H(9A) | 109.9 |
| C(4)-C(9)-H(9B) | 109.9 |
| C(10)-C(9)-H(9B) | 109.9 |
| H(9A)-C(9)-H(9B) | 108.3 |
| C(9)-C(10)-C(7) | 111.03(10) |
| C(9)-C(10)-H(10A) | 109.4 |
| C(7)-C(10)-H(10A) | 109.4 |
| C(9)-C(10)-H(10B) | 109.4 |
| C(7)-C(10)-H(10B) | 109.4 |
| H(10A)-C(10)-H(10B) | 108.0 |
| C(7)-C(11)-C(12) | 111.19(10) |
| C(7)-C(11)-H(11A) | 109.4 |
| C(12)-C(11)-H(11A) | 109.4 |
| C(7)-C(11)-H(11B) | 109.4 |
| C(12)-C(11)-H(11B) | 109.4 |
| H(11A)-C(11)-H(11B) | 108.0 |
| O(3)-C(12)-C(11) | 116.30(10) |
| O(3)-C(12)-H(12A) | 108.2 |
| C(11)-C(12)-H(12A) | 108.2 |
| O(3)-C(12)-H(12B) | 108.2 |
| C(11)-C(12)-H(12B) | 108.2 |
| H(12A)-C(12)-H(12B) | 107.4 |
| O(4)-C(13)-O(3) | 117.35(10) |
| O(4)-C(13)-C(6) | 123.28(11) |
| O(3)-C(13)-C(6) | 119.37(10) |
| O(5)-C(14)-C(15) | 109.29(9) |
| O(5)-C(14)-C(6) | 109.39(9) |
| C(15)-C(14)-C(6) | 115.23(9) |
| O(5)-C(14)-H(14) | 107.5 |
| C(15)-C(14)-H(14) | 107.5 |
| C(6)-C(14)-H(14) | 107.5 |
| C(20)-C(15)-C(16) | 118.81(11) |
| C(20)-C(15)-C(14) | 121.92(11) |
| C(16)-C(15)-C(14) | 119.25(11) |
| C(17)-C(16)-C(15) | 120.84(12) |
| C(17)-C(16)-H(16) | 119.6 |
| C(15)-C(16)-H(16) | 119.6 |
| C(18)-C(17)-C(16) | 119.87(12) |
| C(18)-C(17)-H(17) | 120.1 |
| C(16)-C(17)-H(17) | 120.1 |
| C(17)-C(18)-C(19) | 119.71(12) |
| C(17)-C(18)-H(18) | 120.1 |
| C(19)-C(18)-H(18) | 120.1 |
| C(20)-C(19)-C(18) | 120.50(12) |
| C(20)-C(19)-H(19) | 119.7 |

| | |
|---|---|
| C(18)-C(19)-H(19) | 119.7 |
| C(19)-C(20)-C(15) | 120.26(11) |
| C(19)-C(20)-H(20) | 119.9 |
| C(15)-C(20)-H(20) | 119.9 |

Table C.4l Anisotropic displacement parameters (A^2 x 10^3) for sb353us. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| O(1) | 16(1) | 26(1) | 33(1) | -13(1) | 12(1) | -6(1) |
| O(2) | 20(1) | 30(1) | 26(1) | -12(1) | 9(1) | -1(1) |
| O(3) | 15(1) | 22(1) | 12(1) | 0(1) | 4(1) | -4(1) |
| O(4) | 20(1) | 24(1) | 12(1) | 2(1) | 6(1) | -1(1) |
| O(5) | 11(1) | 23(1) | 15(1) | -1(1) | 6(1) | 0(1) |
| C(1) | 19(1) | 27(1) | 36(1) | -12(1) | 10(1) | -8(1) |
| C(2) | 14(1) | 19(1) | 15(1) | 1(1) | 4(1) | 3(1) |
| C(3) | 13(1) | 17(1) | 15(1) | 0(1) | 5(1) | 2(1) |
| C(4) | 13(1) | 20(1) | 16(1) | -1(1) | 7(1) | 1(1) |
| C(5) | 13(1) | 19(1) | 15(1) | 1(1) | 7(1) | 0(1) |
| C(6) | 12(1) | 16(1) | 11(1) | 0(1) | 5(1) | 0(1) |
| C(7) | 12(1) | 16(1) | 12(1) | 1(1) | 5(1) | 0(1) |
| C(8) | 14(1) | 20(1) | 13(1) | 2(1) | 5(1) | 2(1) |
| C(9) | 18(1) | 21(1) | 18(1) | -3(1) | 8(1) | 1(1) |
| C(10) | 17(1) | 16(1) | 17(1) | -1(1) | 7(1) | 0(1) |
| C(11) | 15(1) | 18(1) | 14(1) | 2(1) | 6(1) | -2(1) |
| C(12) | 15(1) | 22(1) | 16(1) | 3(1) | 6(1) | -3(1) |
| C(13) | 14(1) | 15(1) | 14(1) | -2(1) | 7(1) | 1(1) |
| C(14) | 10(1) | 18(1) | 11(1) | -1(1) | 4(1) | 1(1) |
| C(15) | 13(1) | 18(1) | 15(1) | -2(1) | 8(1) | 1(1) |
| C(16) | 14(1) | 19(1) | 17(1) | -1(1) | 7(1) | 2(1) |
| C(17) | 14(1) | 21(1) | 23(1) | -5(1) | 9(1) | -3(1) |
| C(18) | 20(1) | 18(1) | 27(1) | -1(1) | 16(1) | -2(1) |
| C(19) | 21(1) | 22(1) | 19(1) | 3(1) | 11(1) | 2(1) |
| C(20) | 15(1) | 21(1) | 15(1) | -2(1) | 6(1) | 0(1) |

Table C.5l Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for sb353us.

| | x | y | z | U(eq) |
|---|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| H(5) | 199(18) | 2888(15) | 3071(19) | 38(5) |
| H(1A) | 6881 | 3175 | 4970 | 42 |
| H(1B) | 7964 | 2362 | 5249 | 42 |
| H(1C) | 7334 | 2460 | 6169 | 42 |
| H(3) | 4803 | 281 | 4067 | 19 |
| H(4) | 4736 | 1259 | 2316 | 19 |
| H(5A) | 2908 | 2168 | 1090 | 18 |
| H(5B) | 3512 | 2654 | 2451 | 18 |
| H(8A) | 3216 | 188 | 4485 | 19 |
| H(8B) | 3103 | 1410 | 4520 | 19 |
| H(9A) | 3925 | -424 | 2010 | 22 |
| H(9B) | 3055 | 258 | 842 | 22 |
| H(10A) | 2378 | -726 | 2480 | 21 |
| H(10B) | 1479 | -162 | 1222 | 21 |
| H(11A) | 760 | 1117 | 3463 | 19 |
| H(11B) | 926 | -86 | 3324 | 19 |
| H(12A) | -475 | -125 | 1387 | 21 |
| H(12B) | -986 | 858 | 1799 | 21 |
| H(14) | 2009 | 2611 | 3671 | 16 |
| H(16) | 3480 | 3886 | 4283 | 20 |
| H(17) | 4147 | 5518 | 4061 | 23 |
| H(18) | 3098 | 6421 | 2210 | 24 |
| H(19) | 1419 | 5664 | 569 | 24 |
| H(20) | 740 | 4038 | 790 | 20 |

Table C.6l Torsion angles [deg] for sb353us.

| | |
|---|---|
| C(1)-O(1)-C(2)-O(2) | -1.58(18) |
| C(1)-O(1)-C(2)-C(3) | 178.67(11) |
| O(2)-C(2)-C(3)-C(8) | -10.20(18) |
| O(1)-C(2)-C(3)-C(8) | 169.53(10) |
| O(2)-C(2)-C(3)-C(4) | 113.72(14) |
| O(1)-C(2)-C(3)-C(4) | -66.55(13) |
| C(2)-C(3)-C(4)-C(9) | 169.18(10) |
| C(8)-C(3)-C(4)-C(9) | -65.22(12) |
| C(2)-C(3)-C(4)-C(5) | -71.19(12) |
| C(8)-C(3)-C(4)-C(5) | 54.41(13) |
| C(9)-C(4)-C(5)-C(6) | 56.37(13) |
| C(3)-C(4)-C(5)-C(6) | -61.80(13) |
| C(4)-C(5)-C(6)-C(13) | -112.71(11) |
| C(4)-C(5)-C(6)-C(7) | 5.56(13) |
| C(4)-C(5)-C(6)-C(14) | 128.85(10) |
| C(13)-C(6)-C(7)-C(11) | -60.47(12) |

| | |
|---|---|
| C(5)-C(6)-C(7)-C(11) | 178.95(9) |
| C(14)-C(6)-C(7)-C(11) | 56.69(12) |
| C(13)-C(6)-C(7)-C(8) | 176.59(9) |
| C(5)-C(6)-C(7)-C(8) | 56.01(12) |
| C(14)-C(6)-C(7)-C(8) | -66.25(12) |
| C(13)-C(6)-C(7)-C(10) | 59.62(12) |
| C(5)-C(6)-C(7)-C(10) | -60.96(12) |
| C(14)-C(6)-C(7)-C(10) | 176.78(9) |
| C(11)-C(7)-C(8)-C(3) | 174.85(10) |
| C(10)-C(7)-C(8)-C(3) | 55.16(12) |
| C(6)-C(7)-C(8)-C(3) | -63.61(12) |
| C(2)-C(3)-C(8)-C(7) | 132.04(11) |
| C(4)-C(3)-C(8)-C(7) | 6.79(13) |
| C(5)-C(4)-C(9)-C(10) | -62.95(13) |
| C(3)-C(4)-C(9)-C(10) | 56.71(12) |
| C(4)-C(9)-C(10)-C(7) | 6.51(14) |
| C(11)-C(7)-C(10)-C(9) | 174.98(10) |
| C(8)-C(7)-C(10)-C(9) | -63.95(12) |
| C(6)-C(7)-C(10)-C(9) | 55.02(13) |
| C(8)-C(7)-C(11)-C(12) | 178.36(10) |
| C(10)-C(7)-C(11)-C(12) | -63.64(13) |
| C(6)-C(7)-C(11)-C(12) | 56.49(13) |
| C(13)-O(3)-C(12)-C(11) | -2.65(17) |
| C(7)-C(11)-C(12)-O(3) | -25.13(15) |
| C(12)-O(3)-C(13)-O(4) | 177.36(11) |
| C(12)-O(3)-C(13)-C(6) | -2.92(17) |
| C(5)-C(6)-C(13)-O(4) | -28.02(16) |
| C(7)-C(6)-C(13)-O(4) | -146.17(11) |
| C(14)-C(6)-C(13)-O(4) | 92.92(13) |
| C(5)-C(6)-C(13)-O(3) | 152.28(10) |
| C(7)-C(6)-C(13)-O(3) | 34.13(14) |
| C(14)-C(6)-C(13)-O(3) | -86.78(12) |
| C(13)-C(6)-C(14)-O(5) | 33.43(12) |
| C(5)-C(6)-C(14)-O(5) | 154.89(9) |
| C(7)-C(6)-C(14)-O(5) | -84.57(11) |
| C(13)-C(6)-C(14)-C(15) | -90.15(11) |
| C(5)-C(6)-C(14)-C(15) | 31.31(13) |
| C(7)-C(6)-C(14)-C(15) | 151.85(10) |
| O(5)-C(14)-C(15)-C(20) | -48.66(14) |
| C(6)-C(14)-C(15)-C(20) | 74.98(14) |
| O(5)-C(14)-C(15)-C(16) | 129.64(11) |
| C(6)-C(14)-C(15)-C(16) | -106.72(12) |
| C(20)-C(15)-C(16)-C(17) | 1.02(18) |
| C(14)-C(15)-C(16)-C(17) | -177.34(10) |
| C(15)-C(16)-C(17)-C(18) | -0.15(18) |
| C(16)-C(17)-C(18)-C(19) | -0.96(19) |

| | |
|---|---|
| C(17)-C(18)-C(19)-C(20) | 1.20(19) |
| C(18)-C(19)-C(20)-C(15) | -0.32(19) |
| C(16)-C(15)-C(20)-C(19) | -0.78(18) |
| C(14)-C(15)-C(20)-C(19) | 177.52(11) |

Table C.7l Hydrogen bonds for sb353us [A and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(5)-H(5)...O(4)#1 | 0.87(2) | 1.99(2) | 2.8066(12) | 154.7(18) |

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+1/2,z+1/2

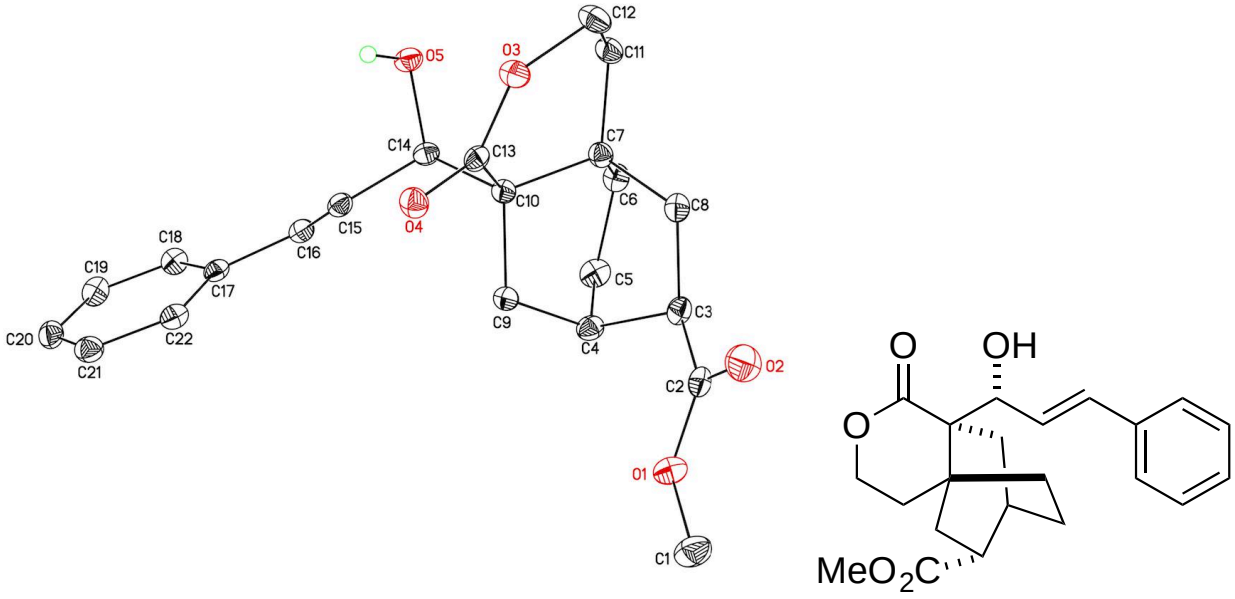



Figure C.13 Structure of yddacin.

**Structure Determination.**

Colorless needles of **yddacin** were grown from a dichloromethane/hexanes solution of the compound at 22 deg. C. A crystal of dimensions 0.24 x 0.20 x 0.15 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (ë = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ù. The exposure times were 1 sec. for the low angle images, 6 sec. for high angle. The integration of the data yielded a total of 14185 reflections to a maximum 2è value of 136.48° of which 3301 were independent and 3108 were greater than 2ó(I). The final cell constants (Table 1) were based on the xyz centroids 10703 reflections above 10ó(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and

refined with the Bruker SHELXTL (version 2014/6) software package, using the space group P1bar with Z = 2 for the formula $C_{22}H_{26}O_5$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in both idealized and refined positions. Full matrix least-squares refinement based on $F^2$ converged at R1 = 0.0453 and wR2 = 0.1045 [based on I > 2sigma(I)], R1 = 0.0471 and wR2 = 0.1065 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.
Sheldrick, G.M. SHELXTL, v. 2014/6; Bruker Analytical X-ray, Madison, WI, 2014.
CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

Table C1m. Crystal data and structure refinement for yddacin.

| | |
|---|---|
| Identification code | yddacin |
| Empirical formula | C22 H26 O5 |
| Formula weight | 370.43 |
| Temperature | 85(2) K |
| Wavelength | 1.54178 A |
| Crystal system, space group | Triclinic, P-1 |
| Unit cell dimensions | a = 7.03930(10) A alpha = 80.368(6) deg. |
| | b = 11.1363(2) A beta = 77.931(6) deg. |
| | c = 12.3739(9) A gamma = 77.748(6) deg. |
| Volume | 919.26(8) A^3 |
| Z, Calculated density | 2, 1.338 Mg/m^3 |
| Absorption coefficient | 0.765 mm^-1 |
| F(000) | 396 |
| Crystal size | 0.240 x 0.200 x 0.150 mm |
| Theta range for data collection | 4.096 to 68.246 deg. |
| Limiting indices | -7<=h<=8, -13<=k<=13, -14<=l<=14 |
| Reflections collected / unique | 14185 / 3301 [R(int) = 0.0611] |
| Completeness to theta = 67.679 | 97.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.891 and 0.772 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 3301 / 0 / 250 |
| Goodness-of-fit on F^2 | 1.046 |
| Final R indices [I>2sigma(I)] | R1 = 0.0453, wR2 = 0.1045 |
| R indices (all data) | R1 = 0.0471, wR2 = 0.1065 |
| Extinction coefficient | 0.037(2) |
| Largest diff. peak and hole | 0.286 and -0.348 e.A^-3 |

Table C2m. Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for yddacin. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| O(1) | 5476(2) | 10913(1) | 2660(1) | 19(1) |
| O(2) | 3411(2) | 10825(1) | 4305(1) | 25(1) |
| O(3) | 2431(2) | 6555(1) | 5341(1) | 16(1) |
| O(4) | 5586(2) | 6387(1) | 4685(1) | 16(1) |
| O(5) | 2750(2) | 4978(1) | 3512(1) | 16(1) |
| C(1) | 6564(2) | 11605(1) | 3125(1) | 23(1) |
| C(2) | 3885(2) | 10583(1) | 3362(1) | 16(1) |
| C(3) | 2737(2) | 9916(1) | 2822(1) | 16(1) |
| C(4) | 4018(2) | 9064(1) | 1981(1) | 16(1) |
| C(5) | 2661(2) | 8698(1) | 1319(1) | 20(1) |
| C(6) | 936(2) | 8204(1) | 2138(1) | 17(1) |
| C(7) | 1420(2) | 7898(1) | 3319(1) | 14(1) |
| C(8) | 1451(2) | 9138(1) | 3715(1) | 15(1) |
| C(9) | 5050(2) | 7900(1) | 2630(1) | 15(1) |
| C(10) | 3524(2) | 7094(1) | 3301(1) | 13(1) |
| C(11) | -115(2) | 7243(1) | 4112(1) | 16(1) |
| C(12) | 337(2) | 6969(1) | 5280(1) | 18(1) |
| C(13) | 3915(2) | 6679(1) | 4489(1) | 13(1) |
| C(14) | 3820(2) | 5850(1) | 2786(1) | 14(1) |
| C(15) | 5947(2) | 5240(1) | 2487(1) | 14(1) |
| C(16) | 6728(2) | 4830(1) | 1513(1) | 15(1) |
| C(17) | 8740(2) | 4108(1) | 1234(1) | 15(1) |
| C(18) | 9152(2) | 3311(1) | 420(1) | 18(1) |
| C(19) | 10991(2) | 2558(1) | 193(1) | 20(1) |
| C(20) | 12465(2) | 2599(1) | 769(1) | 20(1) |
| C(21) | 12092(2) | 3407(1) | 1566(1) | 18(1) |
| C(22) | 10253(2) | 4156(1) | 1793(1) | 17(1) |

Table C.3m Bond lengths [A] and angles [deg] for yddacin.

| | |
|---|---|
| O(1)-C(2) | 1.3429(18) |
| O(1)-C(1) | 1.4471(18) |
| O(2)-C(2) | 1.2049(18) |
| O(3)-C(13) | 1.3322(18) |
| O(3)-C(12) | 1.4621(17) |
| O(4)-C(13) | 1.2160(18) |
| O(5)-C(14) | 1.4330(17) |
| O(5)-H(5) | 0.87(2) |
| C(1)-H(1A) | 0.9800 |
| C(1)-H(1B) | 0.9800 |
| C(1)-H(1C) | 0.9800 |
| C(2)-C(3) | 1.516(2) |

| | |
|---|---|
| C(3)-C(4) | 1.5402(19) |
| C(3)-C(8) | 1.544(2) |
| C(3)-H(3) | 1.0000 |
| C(4)-C(9) | 1.5327(19) |
| C(4)-C(5) | 1.534(2) |
| C(4)-H(4) | 1.0000 |
| C(5)-C(6) | 1.545(2) |
| C(5)-H(5A) | 0.9900 |
| C(5)-H(5B) | 0.9900 |
| C(6)-C(7) | 1.5357(19) |
| C(6)-H(6A) | 0.9900 |
| C(6)-H(6B) | 0.9900 |
| C(7)-C(11) | 1.5210(19) |
| C(7)-C(8) | 1.5461(18) |
| C(7)-C(10) | 1.5574(18) |
| C(8)-H(8A) | 0.9900 |
| C(8)-H(8B) | 0.9900 |
| C(9)-C(10) | 1.5609(19) |
| C(9)-H(9A) | 0.9900 |
| C(9)-H(9B) | 0.9900 |
| C(10)-C(13) | 1.5289(19) |
| C(10)-C(14) | 1.5770(18) |
| C(11)-C(12) | 1.512(2) |
| C(11)-H(11A) | 0.9900 |
| C(11)-H(11B) | 0.9900 |
| C(12)-H(12A) | 0.9900 |
| C(12)-H(12B) | 0.9900 |
| C(14)-C(15) | 1.5034(19) |
| C(14)-H(14) | 1.0000 |
| C(15)-C(16) | 1.328(2) |
| C(15)-H(15) | 0.9500 |
| C(16)-C(17) | 1.475(2) |
| C(16)-H(16) | 0.9500 |
| C(17)-C(18) | 1.397(2) |
| C(17)-C(22) | 1.400(2) |
| C(18)-C(19) | 1.388(2) |
| C(18)-H(18) | 0.9500 |
| C(19)-C(20) | 1.388(2) |
| C(19)-H(19) | 0.9500 |
| C(20)-C(21) | 1.393(2) |
| C(20)-H(20) | 0.9500 |
| C(21)-C(22) | 1.385(2) |
| C(21)-H(21) | 0.9500 |
| C(22)-H(22) | 0.9500 |
| C(2)-O(1)-C(1) | 114.44(11) |
| C(13)-O(3)-C(12) | 124.80(11) |

| | |
|---|---|
| C(14)-O(5)-H(5) | 107.0(15) |
| O(1)-C(1)-H(1A) | 109.5 |
| O(1)-C(1)-H(1B) | 109.5 |
| H(1A)-C(1)-H(1B) | 109.5 |
| O(1)-C(1)-H(1C) | 109.5 |
| H(1A)-C(1)-H(1C) | 109.5 |
| H(1B)-C(1)-H(1C) | 109.5 |
| O(2)-C(2)-O(1) | 123.09(13) |
| O(2)-C(2)-C(3) | 124.31(14) |
| O(1)-C(2)-C(3) | 112.58(12) |
| C(2)-C(3)-C(4) | 114.76(12) |
| C(2)-C(3)-C(8) | 110.77(11) |
| C(4)-C(3)-C(8) | 108.29(11) |
| C(2)-C(3)-H(3) | 107.6 |
| C(4)-C(3)-H(3) | 107.6 |
| C(8)-C(3)-H(3) | 107.6 |
| C(9)-C(4)-C(5) | 109.56(12) |
| C(9)-C(4)-C(3) | 108.40(11) |
| C(5)-C(4)-C(3) | 108.46(12) |
| C(9)-C(4)-H(4) | 110.1 |
| C(5)-C(4)-H(4) | 110.1 |
| C(3)-C(4)-H(4) | 110.1 |
| C(4)-C(5)-C(6) | 109.24(11) |
| C(4)-C(5)-H(5A) | 109.8 |
| C(6)-C(5)-H(5A) | 109.8 |
| C(4)-C(5)-H(5B) | 109.8 |
| C(6)-C(5)-H(5B) | 109.8 |
| H(5A)-C(5)-H(5B) | 108.3 |
| C(7)-C(6)-C(5) | 110.00(12) |
| C(7)-C(6)-H(6A) | 109.7 |
| C(5)-C(6)-H(6A) | 109.7 |
| C(7)-C(6)-H(6B) | 109.7 |
| C(5)-C(6)-H(6B) | 109.7 |
| H(6A)-C(6)-H(6B) | 108.2 |
| C(11)-C(7)-C(6) | 111.18(11) |
| C(11)-C(7)-C(8) | 110.14(11) |
| C(6)-C(7)-C(8) | 107.22(11) |
| C(11)-C(7)-C(10) | 110.45(11) |
| C(6)-C(7)-C(10) | 110.52(11) |
| C(8)-C(7)-C(10) | 107.19(11) |
| C(3)-C(8)-C(7) | 110.80(11) |
| C(3)-C(8)-H(8A) | 109.5 |
| C(7)-C(8)-H(8A) | 109.5 |
| C(3)-C(8)-H(8B) | 109.5 |
| C(7)-C(8)-H(8B) | 109.5 |
| H(8A)-C(8)-H(8B) | 108.1 |

| | |
|---|---|
| C(4)-C(9)-C(10) | 110.82(11) |
| C(4)-C(9)-H(9A) | 109.5 |
| C(10)-C(9)-H(9A) | 109.5 |
| C(4)-C(9)-H(9B) | 109.5 |
| C(10)-C(9)-H(9B) | 109.5 |
| H(9A)-C(9)-H(9B) | 108.1 |
| C(13)-C(10)-C(7) | 110.33(11) |
| C(13)-C(10)-C(9) | 110.19(11) |
| C(7)-C(10)-C(9) | 107.81(11) |
| C(13)-C(10)-C(14) | 104.51(10) |
| C(7)-C(10)-C(14) | 113.80(11) |
| C(9)-C(10)-C(14) | 110.19(11) |
| C(12)-C(11)-C(7) | 111.14(12) |
| C(12)-C(11)-H(11A) | 109.4 |
| C(7)-C(11)-H(11A) | 109.4 |
| C(12)-C(11)-H(11B) | 109.4 |
| C(7)-C(11)-H(11B) | 109.4 |
| H(11A)-C(11)-H(11B) | 108.0 |
| O(3)-C(12)-C(11) | 114.82(11) |
| O(3)-C(12)-H(12A) | 108.6 |
| C(11)-C(12)-H(12A) | 108.6 |
| O(3)-C(12)-H(12B) | 108.6 |
| C(11)-C(12)-H(12B) | 108.6 |
| H(12A)-C(12)-H(12B) | 107.5 |
| O(4)-C(13)-O(3) | 117.45(12) |
| O(4)-C(13)-C(10) | 121.58(12) |
| O(3)-C(13)-C(10) | 120.86(12) |
| O(5)-C(14)-C(15) | 109.07(11) |
| O(5)-C(14)-C(10) | 111.55(11) |
| C(15)-C(14)-C(10) | 113.93(11) |
| O(5)-C(14)-H(14) | 107.3 |
| C(15)-C(14)-H(14) | 107.3 |
| C(10)-C(14)-H(14) | 107.3 |
| C(16)-C(15)-C(14) | 123.48(13) |
| C(16)-C(15)-H(15) | 118.3 |
| C(14)-C(15)-H(15) | 118.3 |
| C(15)-C(16)-C(17) | 124.99(13) |
| C(15)-C(16)-H(16) | 117.5 |
| C(17)-C(16)-H(16) | 117.5 |
| C(18)-C(17)-C(22) | 118.25(13) |
| C(18)-C(17)-C(16) | 119.79(13) |
| C(22)-C(17)-C(16) | 121.92(13) |
| C(19)-C(18)-C(17) | 121.11(14) |
| C(19)-C(18)-H(18) | 119.4 |
| C(17)-C(18)-H(18) | 119.4 |
| C(18)-C(19)-C(20) | 119.97(14) |

| | |
|---|---|
| C(18)-C(19)-H(19) | 120.0 |
| C(20)-C(19)-H(19) | 120.0 |
| C(19)-C(20)-C(21) | 119.65(14) |
| C(19)-C(20)-H(20) | 120.2 |
| C(21)-C(20)-H(20) | 120.2 |
| C(22)-C(21)-C(20) | 120.25(14) |
| C(22)-C(21)-H(21) | 119.9 |
| C(20)-C(21)-H(21) | 119.9 |
| C(21)-C(22)-C(17) | 120.75(13) |
| C(21)-C(22)-H(22) | 119.6 |
| C(17)-C(22)-H(22) | 119.6 |

Table C.4m Anisotropic displacement parameters (A^2 x 10^3) for yddacin. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| O(1) | 22(1) | 19(1) | 20(1) | -2(1) | -4(1) | -8(1) |
| O(2) | 26(1) | 26(1) | 25(1) | -12(1) | -1(1) | -6(1) |
| O(3) | 14(1) | 18(1) | 14(1) | 0(1) | -3(1) | -4(1) |
| O(4) | 14(1) | 17(1) | 18(1) | -3(1) | -6(1) | -2(1) |
| O(5) | 17(1) | 15(1) | 18(1) | 0(1) | -4(1) | -6(1) |
| C(1) | 25(1) | 21(1) | 27(1) | -3(1) | -9(1) | -9(1) |
| C(2) | 16(1) | 11(1) | 20(1) | -1(1) | -4(1) | 1(1) |
| C(3) | 17(1) | 12(1) | 17(1) | -1(1) | -4(1) | -1(1) |
| C(4) | 19(1) | 15(1) | 14(1) | -1(1) | -1(1) | -5(1) |
| C(5) | 25(1) | 21(1) | 14(1) | -1(1) | -5(1) | -6(1) |
| C(6) | 18(1) | 17(1) | 16(1) | -2(1) | -6(1) | -2(1) |
| C(7) | 12(1) | 14(1) | 15(1) | -2(1) | -3(1) | -2(1) |
| C(8) | 16(1) | 14(1) | 15(1) | -3(1) | -3(1) | -1(1) |
| C(9) | 13(1) | 14(1) | 18(1) | -3(1) | -1(1) | -3(1) |
| C(10) | 12(1) | 13(1) | 14(1) | -2(1) | -2(1) | -3(1) |
| C(11) | 12(1) | 18(1) | 18(1) | -2(1) | -3(1) | -3(1) |
| C(12) | 12(1) | 24(1) | 18(1) | 0(1) | -1(1) | -4(1) |
| C(13) | 15(1) | 10(1) | 16(1) | -4(1) | -3(1) | -3(1) |
| C(14) | 15(1) | 14(1) | 14(1) | -1(1) | -3(1) | -5(1) |
| C(15) | 16(1) | 12(1) | 17(1) | -1(1) | -5(1) | -4(1) |
| C(16) | 17(1) | 14(1) | 16(1) | 0(1) | -4(1) | -4(1) |
| C(17) | 18(1) | 13(1) | 13(1) | 1(1) | -1(1) | -5(1) |
| C(18) | 21(1) | 19(1) | 13(1) | -2(1) | -4(1) | -4(1) |
| C(19) | 26(1) | 18(1) | 13(1) | -3(1) | -1(1) | -2(1) |
| C(20) | 19(1) | 18(1) | 17(1) | 1(1) | 0(1) | 0(1) |
| C(21) | 19(1) | 20(1) | 17(1) | 1(1) | -4(1) | -6(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(22) | 20(1) | 15(1) | 15(1) | -2(1) | -2(1) | -5(1) |

Table C.5m Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for yddacin.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(5) | 3500(30) | 4580(20) | 3984(19) | 35(5) |
| H(1A) | 5723 | 12395 | 3302 | 35 |
| H(1B) | 7742 | 11765 | 2581 | 35 |
| H(1C) | 6965 | 11125 | 3806 | 35 |
| H(3) | 1827 | 10560 | 2413 | 19 |
| H(4) | 5021 | 9504 | 1465 | 19 |
| H(5A) | 3419 | 8050 | 856 | 23 |
| H(5B) | 2136 | 9427 | 818 | 23 |
| H(6A) | -288 | 8836 | 2138 | 20 |
| H(6B) | 710 | 7449 | 1897 | 20 |
| H(8A) | 85 | 9612 | 3868 | 18 |
| H(8B) | 1984 | 8970 | 4416 | 18 |
| H(9A) | 5751 | 8145 | 3150 | 18 |
| H(9B) | 6042 | 7406 | 2104 | 18 |
| H(11A) | -1439 | 7771 | 4121 | 19 |
| H(11B) | -136 | 6458 | 3843 | 19 |
| H(12A) | -159 | 7727 | 5649 | 22 |
| H(12B) | -397 | 6322 | 5704 | 22 |
| H(14) | 3264 | 6057 | 2083 | 16 |
| H(15) | 6776 | 5143 | 3022 | 17 |
| H(16) | 5932 | 5017 | 953 | 18 |
| H(18) | 8156 | 3286 | 16 | 21 |
| H(19) | 11241 | 2014 | -356 | 24 |
| H(20) | 13722 | 2078 | 620 | 23 |
| H(21) | 13102 | 3445 | 1955 | 22 |
| H(22) | 10015 | 4708 | 2334 | 20 |

Table C.6m Torsion angles [deg] for yddacin.

| | |
|---|---|
| C(1)-O(1)-C(2)-O(2) | -1.03(19) |
| C(1)-O(1)-C(2)-C(3) | 177.20(11) |
| O(2)-C(2)-C(3)-C(4) | -146.09(14) |
| O(1)-C(2)-C(3)-C(4) | 35.70(16) |
| O(2)-C(2)-C(3)-C(8) | -23.10(19) |

| | |
|---|---|
| O(1)-C(2)-C(3)-C(8) | 158.70(11) |
| C(2)-C(3)-C(4)-C(9) | 73.97(15) |
| C(8)-C(3)-C(4)-C(9) | -50.34(15) |
| C(2)-C(3)-C(4)-C(5) | -167.14(11) |
| C(8)-C(3)-C(4)-C(5) | 68.55(14) |
| C(9)-C(4)-C(5)-C(6) | 67.34(15) |
| C(3)-C(4)-C(5)-C(6) | -50.81(15) |
| C(4)-C(5)-C(6)-C(7) | -15.61(15) |
| C(5)-C(6)-C(7)-C(11) | -172.04(11) |
| C(5)-C(6)-C(7)-C(8) | 67.51(14) |
| C(5)-C(6)-C(7)-C(10) | -49.01(15) |
| C(2)-C(3)-C(8)-C(7) | -142.13(12) |
| C(4)-C(3)-C(8)-C(7) | -15.46(16) |
| C(11)-C(7)-C(8)-C(3) | -170.49(11) |
| C(6)-C(7)-C(8)-C(3) | -49.38(15) |
| C(10)-C(7)-C(8)-C(3) | 69.31(14) |
| C(5)-C(4)-C(9)-C(10) | -49.97(15) |
| C(3)-C(4)-C(9)-C(10) | 68.22(14) |
| C(11)-C(7)-C(10)-C(13) | -50.64(14) |
| C(6)-C(7)-C(10)-C(13) | -174.10(11) |
| C(8)-C(7)-C(10)-C(13) | 69.37(13) |
| C(11)-C(7)-C(10)-C(9) | -171.00(11) |
| C(6)-C(7)-C(10)-C(9) | 65.53(14) |
| C(8)-C(7)-C(10)-C(9) | -51.00(14) |
| C(11)-C(7)-C(10)-C(14) | 66.46(14) |
| C(6)-C(7)-C(10)-C(14) | -57.00(15) |
| C(8)-C(7)-C(10)-C(14) | -173.54(11) |
| C(4)-C(9)-C(10)-C(13) | -134.25(12) |
| C(4)-C(9)-C(10)-C(7) | -13.79(15) |
| C(4)-C(9)-C(10)-C(14) | 110.94(12) |
| C(6)-C(7)-C(11)-C(12) | -178.68(11) |
| C(8)-C(7)-C(11)-C(12) | -59.97(15) |
| C(10)-C(7)-C(11)-C(12) | 58.25(15) |
| C(13)-O(3)-C(12)-C(11) | 16.15(19) |
| C(7)-C(11)-C(12)-O(3) | -40.11(16) |
| C(12)-O(3)-C(13)-O(4) | 173.91(12) |
| C(12)-O(3)-C(13)-C(10) | -9.98(19) |
| C(7)-C(10)-C(13)-O(4) | -156.99(12) |
| C(9)-C(10)-C(13)-O(4) | -38.06(16) |
| C(14)-C(10)-C(13)-O(4) | 80.30(15) |
| C(7)-C(10)-C(13)-O(3) | 27.06(16) |
| C(9)-C(10)-C(13)-O(3) | 145.98(12) |
| C(14)-C(10)-C(13)-O(3) | -95.65(14) |
| C(13)-C(10)-C(14)-O(5) | 49.11(14) |
| C(7)-C(10)-C(14)-O(5) | -71.31(14) |
| C(9)-C(10)-C(14)-O(5) | 167.47(11) |

| | |
|---|---|
| C(13)-C(10)-C(14)-C(15) | -74.92(14) |
| C(7)-C(10)-C(14)-C(15) | 164.66(11) |
| C(9)-C(10)-C(14)-C(15) | 43.44(15) |
| O(5)-C(14)-C(15)-C(16) | 102.72(15) |
| C(10)-C(14)-C(15)-C(16) | -131.92(14) |
| C(14)-C(15)-C(16)-C(17) | -172.91(12) |
| C(15)-C(16)-C(17)-C(18) | 153.87(14) |
| C(15)-C(16)-C(17)-C(22) | -23.6(2) |
| C(22)-C(17)-C(18)-C(19) | 2.0(2) |
| C(16)-C(17)-C(18)-C(19) | -175.59(13) |
| C(17)-C(18)-C(19)-C(20) | -0.8(2) |
| C(18)-C(19)-C(20)-C(21) | -0.6(2) |
| C(19)-C(20)-C(21)-C(22) | 0.8(2) |
| C(20)-C(21)-C(22)-C(17) | 0.4(2) |
| C(18)-C(17)-C(22)-C(21) | -1.8(2) |
| C(16)-C(17)-C(22)-C(21) | 175.73(13) |

Table C.7m Hydrogen bonds for yddacin [A and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(5)-H(5)...O(4)#1 | 0.87(2) | 1.96(2) | 2.8041(14) | 163(2) |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1

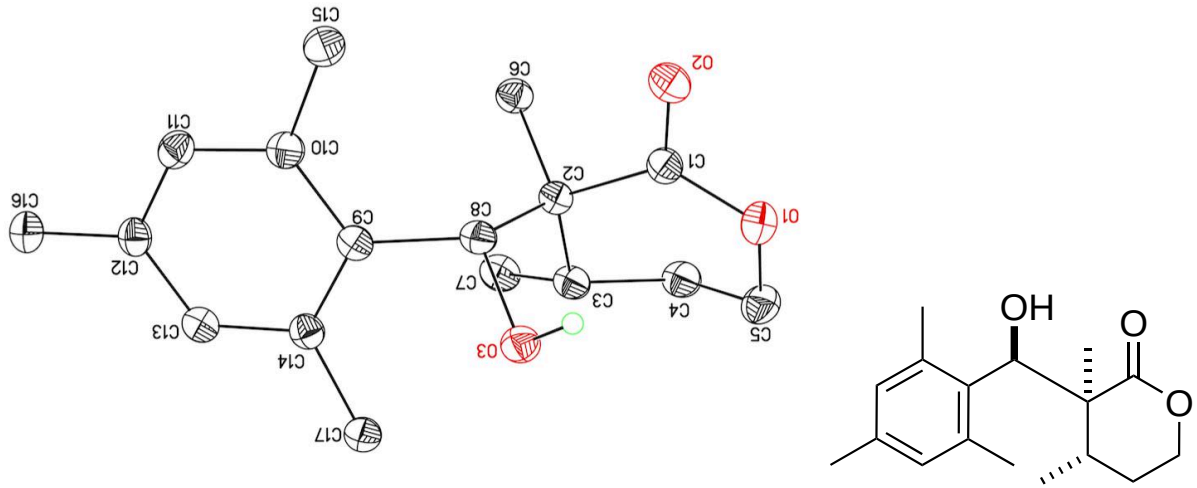



Figure C.14 Structure of ydbmes.

**Structure Determination.**

Colorless block-like crystals of **ydbmes** were grown from a dichloromethane/hexanes solution of the compound at 22 deg. C. A crystal of dimensions 0.20 x 0.16 x 0.16 mm was

mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (ë = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ù. The exposure times were 2 sec. for the low angle images, 12 sec. for high angle. The integration of the data yielded a total of 23084 reflections to a maximum 2è value of 136.38° of which 5301 were independent and 4660 were greater than 2ó(I). The final cell constants (Table 1) were based on the xyz centroids 15374 reflections above 10ó(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group P1bar with Z = 4 for the formula $C_{17}H_{24}O_3$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in both idealized and refined positions. There are two crystallographically independent molecules in the asymmetric unit. Full matrix least-squares refinement based on $F^2$ converged at R1 = 0.0460 and wR2 = 0.1293 [based on I > 2sigma(I)], R1 = 0.0501 and wR2 = 0.1342 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.
Sheldrick, G.M. SHELXTL, v. 2014/6; Bruker Analytical X-ray, Madison, WI, 2014.
CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

Table C.1n Crystal data and structure refinement for ydbmes.

| | |
|---|---|
| Identification code | ydbmes |
| Empirical formula | C17 H24 O3 |
| Formula weight | 276.36 |
| Temperature | 85(2) K |
| Wavelength | 1.54178 A |
| Crystal system, space group | Triclinic, P-1 |
| Unit cell dimensions | a = 8.13540(10) A alpha = 115.337(8) deg. |
| | b = 14.2018(3) A beta = 95.580(7) deg. |
| | c = 14.9161(11) A gamma = 103.266(7) deg. |
| Volume | 1478.14(15) A^3 |
| Z, Calculated density | 4, 1.242 Mg/m^3 |
| Absorption coefficient | 0.665 mm^-1 |
| F(000) | 600 |
| Crystal size | 0.200 x 0.160 x 0.160 mm |
| Theta range for data collection | 3.362 to 68.189 deg. |
| Limiting indices | -9<=h<=9, -17<=k<=17, -17<=l<=17 |
| Reflections collected / unique | 23084 / 5301 [R(int) = 0.0501] |
| Completeness to theta = 67.679 | 98.2 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.000 and 0.782 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 5301 / 0 / 380 |
| Goodness-of-fit on F^2 | 1.125 |

Final R indices [I>2sigma(I)] R1 = 0.0460, wR2 = 0.1293
R indices (all data) R1 = 0.0501, wR2 = 0.1342
Extinction coefficient 0.0021(5)
Largest diff. peak and hole 0.233 and -0.256 e.A^-3

Table C.2n Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for ydbmes. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 4616(1) | 6684(1) | 5625(1) | 24(1) |
| O(2) | 6593(1) | 5953(1) | 5017(1) | 23(1) |
| O(3) | 5316(1) | 5322(1) | 6917(1) | 21(1) |
| O(4) | 7657(1) | 8462(1) | 5195(1) | 25(1) |
| O(5) | 5113(2) | 8690(1) | 5207(1) | 27(1) |
| O(6) | 6962(1) | 9972(1) | 4112(1) | 22(1) |
| C(1) | 6124(2) | 6497(1) | 5774(1) | 19(1) |
| C(2) | 7225(2) | 6884(1) | 6836(1) | 19(1) |
| C(3) | 6581(2) | 7696(1) | 7707(1) | 21(1) |
| C(4) | 5593(2) | 8270(1) | 7296(1) | 25(1) |
| C(5) | 4065(2) | 7440(1) | 6473(1) | 27(1) |
| C(6) | 9088(2) | 7417(1) | 6814(1) | 21(1) |
| C(7) | 8001(2) | 8528(1) | 8645(1) | 27(1) |
| C(8) | 7052(2) | 5764(1) | 6867(1) | 19(1) |
| C(9) | 8385(2) | 5786(1) | 7676(1) | 18(1) |
| C(10) | 9840(2) | 5449(1) | 7369(1) | 20(1) |
| C(11) | 11141(2) | 5493(1) | 8081(1) | 22(1) |
| C(12) | 11039(2) | 5825(1) | 9092(1) | 20(1) |
| C(13) | 9559(2) | 6083(1) | 9362(1) | 21(1) |
| C(14) | 8232(2) | 6071(1) | 8685(1) | 19(1) |
| C(15) | 10021(2) | 4974(1) | 6274(1) | 25(1) |
| C(16) | 12483(2) | 5911(1) | 9862(1) | 25(1) |
| C(17) | 6684(2) | 6335(1) | 9110(1) | 24(1) |
| C(18) | 6158(2) | 8420(1) | 4696(1) | 21(1) |
| C(19) | 5749(2) | 8050(1) | 3546(1) | 19(1) |
| C(20) | 7233(2) | 7720(1) | 3026(1) | 19(1) |
| C(21) | 8205(2) | 7259(1) | 3587(1) | 22(1) |
| C(22) | 8985(2) | 8119(1) | 4661(1) | 25(1) |
| C(23) | 4068(2) | 7083(1) | 3098(1) | 23(1) |
| C(24) | 6651(2) | 6918(1) | 1895(1) | 25(1) |
| C(25) | 5413(2) | 9082(1) | 3514(1) | 18(1) |
| C(26) | 4793(2) | 8995(1) | 2475(1) | 18(1) |
| C(27) | 2990(2) | 8772(1) | 2137(1) | 19(1) |
| C(28) | 2332(2) | 8658(1) | 1191(1) | 21(1) |

| | | | | |
|---|---|---|---|---|
| C(29) | 3391(2) | 8762(1) | 538(1) | 22(1) |
| C(30) | 5157(2) | 9034(1) | 896(1) | 22(1) |
| C(31) | 5890(2) | 9177(1) | 1848(1) | 21(1) |
| C(32) | 1713(2) | 8692(1) | 2793(1) | 25(1) |
| C(33) | 2649(2) | 8585(1) | -504(1) | 28(1) |
| C(34) | 7848(2) | 9526(1) | 2113(1) | 26(1) |

Table C.3n Bond lengths [A] and angles [deg] for ydbmes.

| | |
|---|---|
| O(1)-C(1) | 1.3317(18) |
| O(1)-C(5) | 1.457(2) |
| O(2)-C(1) | 1.2202(18) |
| O(3)-C(8) | 1.4316(17) |
| O(3)-H(3) | 0.99(3) |
| O(4)-C(18) | 1.3406(19) |
| O(4)-C(22) | 1.4541(18) |
| O(5)-C(18) | 1.2149(18) |
| O(6)-C(25) | 1.4372(19) |
| O(6)-H(6) | 0.86(2) |
| C(1)-C(2) | 1.538(2) |
| C(2)-C(6) | 1.541(2) |
| C(2)-C(3) | 1.556(2) |
| C(2)-C(8) | 1.585(2) |
| C(3)-C(4) | 1.524(2) |
| C(3)-C(7) | 1.527(2) |
| C(3)-H(3A) | 1.0000 |
| C(4)-C(5) | 1.495(3) |
| C(4)-H(4A) | 0.9900 |
| C(4)-H(4B) | 0.9900 |
| C(5)-H(5A) | 0.9900 |
| C(5)-H(5B) | 0.9900 |
| C(6)-H(6A) | 0.9800 |
| C(6)-H(6B) | 0.9800 |
| C(6)-H(6C) | 0.9800 |
| C(7)-H(7A) | 0.9800 |
| C(7)-H(7B) | 0.9800 |
| C(7)-H(7C) | 0.9800 |
| C(8)-C(9) | 1.526(2) |
| C(8)-H(8) | 1.0000 |
| C(9)-C(14) | 1.409(2) |
| C(9)-C(10) | 1.420(2) |
| C(10)-C(11) | 1.396(2) |
| C(10)-C(15) | 1.515(2) |

| | |
|---|---|
| C(11)-C(12) | 1.392(2) |
| C(11)-H(11) | 0.9500 |
| C(12)-C(13) | 1.384(2) |
| C(12)-C(16) | 1.505(2) |
| C(13)-C(14) | 1.397(2) |
| C(13)-H(13) | 0.9500 |
| C(14)-C(17) | 1.516(2) |
| C(15)-H(15A) | 0.9800 |
| C(15)-H(15B) | 0.9800 |
| C(15)-H(15C) | 0.9800 |
| C(16)-H(16A) | 0.9800 |
| C(16)-H(16B) | 0.9800 |
| C(16)-H(16C) | 0.9800 |
| C(17)-H(17A) | 0.9800 |
| C(17)-H(17B) | 0.9800 |
| C(17)-H(17C) | 0.9800 |
| C(18)-C(19) | 1.539(2) |
| C(19)-C(23) | 1.542(2) |
| C(19)-C(20) | 1.5521(19) |
| C(19)-C(25) | 1.5699(19) |
| C(20)-C(24) | 1.524(2) |
| C(20)-C(21) | 1.526(2) |
| C(20)-H(20) | 1.0000 |
| C(21)-C(22) | 1.495(2) |
| C(21)-H(21A) | 0.9900 |
| C(21)-H(21B) | 0.9900 |
| C(22)-H(22A) | 0.9900 |
| C(22)-H(22B) | 0.9900 |
| C(23)-H(23A) | 0.9800 |
| C(23)-H(23B) | 0.9800 |
| C(23)-H(23C) | 0.9800 |
| C(24)-H(24A) | 0.9800 |
| C(24)-H(24B) | 0.9800 |
| C(24)-H(24C) | 0.9800 |
| C(25)-C(26) | 1.526(2) |
| C(25)-H(25) | 1.0000 |
| C(26)-C(31) | 1.415(2) |
| C(26)-C(27) | 1.419(2) |
| C(27)-C(28) | 1.387(2) |
| C(27)-C(32) | 1.513(2) |
| C(28)-C(29) | 1.393(2) |
| C(28)-H(28) | 0.9500 |
| C(29)-C(30) | 1.385(2) |
| C(29)-C(33) | 1.502(2) |
| C(30)-C(31) | 1.395(2) |
| C(30)-H(30) | 0.9500 |

| | |
|---|---|
| C(31)-C(34) | 1.512(2) |
| C(32)-H(32A) | 0.9800 |
| C(32)-H(32B) | 0.9800 |
| C(32)-H(32C) | 0.9800 |
| C(33)-H(33A) | 0.9800 |
| C(33)-H(33B) | 0.9800 |
| C(33)-H(33C) | 0.9800 |
| C(34)-H(34A) | 0.9800 |
| C(34)-H(34B) | 0.9800 |
| C(34)-H(34C) | 0.9800 |
| C(1)-O(1)-C(5) | 120.47(13) |
| C(8)-O(3)-H(3) | 103.3(15) |
| C(18)-O(4)-C(22) | 121.22(12) |
| C(25)-O(6)-H(6) | 104.5(16) |
| O(2)-C(1)-O(1) | 116.85(14) |
| O(2)-C(1)-C(2) | 119.78(13) |
| O(1)-C(1)-C(2) | 123.30(13) |
| C(1)-C(2)-C(6) | 105.65(12) |
| C(1)-C(2)-C(3) | 112.91(12) |
| C(6)-C(2)-C(3) | 111.28(13) |
| C(1)-C(2)-C(8) | 101.91(12) |
| C(6)-C(2)-C(8) | 111.28(11) |
| C(3)-C(2)-C(8) | 113.22(11) |
| C(4)-C(3)-C(7) | 110.68(13) |
| C(4)-C(3)-C(2) | 109.59(12) |
| C(7)-C(3)-C(2) | 114.61(13) |
| C(4)-C(3)-H(3A) | 107.2 |
| C(7)-C(3)-H(3A) | 107.2 |
| C(2)-C(3)-H(3A) | 107.2 |
| C(5)-C(4)-C(3) | 109.35(13) |
| C(5)-C(4)-H(4A) | 109.8 |
| C(3)-C(4)-H(4A) | 109.8 |
| C(5)-C(4)-H(4B) | 109.8 |
| C(3)-C(4)-H(4B) | 109.8 |
| H(4A)-C(4)-H(4B) | 108.3 |
| O(1)-C(5)-C(4) | 110.84(12) |
| O(1)-C(5)-H(5A) | 109.5 |
| C(4)-C(5)-H(5A) | 109.5 |
| O(1)-C(5)-H(5B) | 109.5 |
| C(4)-C(5)-H(5B) | 109.5 |
| H(5A)-C(5)-H(5B) | 108.1 |
| C(2)-C(6)-H(6A) | 109.5 |
| C(2)-C(6)-H(6B) | 109.5 |
| H(6A)-C(6)-H(6B) | 109.5 |
| C(2)-C(6)-H(6C) | 109.5 |
| H(6A)-C(6)-H(6C) | 109.5 |

| | |
|---|---|
| H(6B)-C(6)-H(6C) | 109.5 |
| C(3)-C(7)-H(7A) | 109.5 |
| C(3)-C(7)-H(7B) | 109.5 |
| H(7A)-C(7)-H(7B) | 109.5 |
| C(3)-C(7)-H(7C) | 109.5 |
| H(7A)-C(7)-H(7C) | 109.5 |
| H(7B)-C(7)-H(7C) | 109.5 |
| O(3)-C(8)-C(9) | 111.91(11) |
| O(3)-C(8)-C(2) | 108.93(11) |
| C(9)-C(8)-C(2) | 116.55(12) |
| O(3)-C(8)-H(8) | 106.3 |
| C(9)-C(8)-H(8) | 106.3 |
| C(2)-C(8)-H(8) | 106.3 |
| C(14)-C(9)-C(10) | 118.16(13) |
| C(14)-C(9)-C(8) | 124.59(13) |
| C(10)-C(9)-C(8) | 117.19(12) |
| C(11)-C(10)-C(9) | 120.02(14) |
| C(11)-C(10)-C(15) | 116.87(13) |
| C(9)-C(10)-C(15) | 123.02(14) |
| C(12)-C(11)-C(10) | 121.95(14) |
| C(12)-C(11)-H(11) | 119.0 |
| C(10)-C(11)-H(11) | 119.0 |
| C(13)-C(12)-C(11) | 117.19(14) |
| C(13)-C(12)-C(16) | 121.41(14) |
| C(11)-C(12)-C(16) | 121.40(13) |
| C(12)-C(13)-C(14) | 123.17(14) |
| C(12)-C(13)-H(13) | 118.4 |
| C(14)-C(13)-H(13) | 118.4 |
| C(13)-C(14)-C(9) | 119.27(13) |
| C(13)-C(14)-C(17) | 115.49(13) |
| C(9)-C(14)-C(17) | 125.19(14) |
| C(10)-C(15)-H(15A) | 109.5 |
| C(10)-C(15)-H(15B) | 109.5 |
| H(15A)-C(15)-H(15B) | 109.5 |
| C(10)-C(15)-H(15C) | 109.5 |
| H(15A)-C(15)-H(15C) | 109.5 |
| H(15B)-C(15)-H(15C) | 109.5 |
| C(12)-C(16)-H(16A) | 109.5 |
| C(12)-C(16)-H(16B) | 109.5 |
| H(16A)-C(16)-H(16B) | 109.5 |
| C(12)-C(16)-H(16C) | 109.5 |
| H(16A)-C(16)-H(16C) | 109.5 |
| H(16B)-C(16)-H(16C) | 109.5 |
| C(14)-C(17)-H(17A) | 109.5 |
| C(14)-C(17)-H(17B) | 109.5 |
| H(17A)-C(17)-H(17B) | 109.5 |

| | |
|---|---|
| C(14)-C(17)-H(17C) | 109.5 |
| H(17A)-C(17)-H(17C) | 109.5 |
| H(17B)-C(17)-H(17C) | 109.5 |
| O(5)-C(18)-O(4) | 115.96(14) |
| O(5)-C(18)-C(19) | 121.06(14) |
| O(4)-C(18)-C(19) | 122.98(12) |
| C(18)-C(19)-C(23) | 105.75(12) |
| C(18)-C(19)-C(20) | 113.25(12) |
| C(23)-C(19)-C(20) | 111.31(12) |
| C(18)-C(19)-C(25) | 101.92(11) |
| C(23)-C(19)-C(25) | 110.97(12) |
| C(20)-C(19)-C(25) | 113.05(11) |
| C(24)-C(20)-C(21) | 110.18(12) |
| C(24)-C(20)-C(19) | 114.54(13) |
| C(21)-C(20)-C(19) | 109.51(12) |
| C(24)-C(20)-H(20) | 107.4 |
| C(21)-C(20)-H(20) | 107.4 |
| C(19)-C(20)-H(20) | 107.4 |
| C(22)-C(21)-C(20) | 109.30(12) |
| C(22)-C(21)-H(21A) | 109.8 |
| C(20)-C(21)-H(21A) | 109.8 |
| C(22)-C(21)-H(21B) | 109.8 |
| C(20)-C(21)-H(21B) | 109.8 |
| H(21A)-C(21)-H(21B) | 108.3 |
| O(4)-C(22)-C(21) | 111.15(13) |
| O(4)-C(22)-H(22A) | 109.4 |
| C(21)-C(22)-H(22A) | 109.4 |
| O(4)-C(22)-H(22B) | 109.4 |
| C(21)-C(22)-H(22B) | 109.4 |
| H(22A)-C(22)-H(22B) | 108.0 |
| C(19)-C(23)-H(23A) | 109.5 |
| C(19)-C(23)-H(23B) | 109.5 |
| H(23A)-C(23)-H(23B) | 109.5 |
| C(19)-C(23)-H(23C) | 109.5 |
| H(23A)-C(23)-H(23C) | 109.5 |
| H(23B)-C(23)-H(23C) | 109.5 |
| C(20)-C(24)-H(24A) | 109.5 |
| C(20)-C(24)-H(24B) | 109.5 |
| H(24A)-C(24)-H(24B) | 109.5 |
| C(20)-C(24)-H(24C) | 109.5 |
| H(24A)-C(24)-H(24C) | 109.5 |
| H(24B)-C(24)-H(24C) | 109.5 |
| O(6)-C(25)-C(26) | 113.47(11) |
| O(6)-C(25)-C(19) | 105.85(11) |
| C(26)-C(25)-C(19) | 117.81(12) |
| O(6)-C(25)-H(25) | 106.3 |

| | |
|---|---|
| C(26)-C(25)-H(25) | 106.3 |
| C(19)-C(25)-H(25) | 106.3 |
| C(31)-C(26)-C(27) | 117.54(14) |
| C(31)-C(26)-C(25) | 124.85(13) |
| C(27)-C(26)-C(25) | 117.52(12) |
| C(28)-C(27)-C(26) | 120.61(13) |
| C(28)-C(27)-C(32) | 116.93(13) |
| C(26)-C(27)-C(32) | 122.41(14) |
| C(27)-C(28)-C(29) | 122.16(14) |
| C(27)-C(28)-H(28) | 118.9 |
| C(29)-C(28)-H(28) | 118.9 |
| C(30)-C(29)-C(28) | 116.75(14) |
| C(30)-C(29)-C(33) | 121.78(14) |
| C(28)-C(29)-C(33) | 121.47(14) |
| C(29)-C(30)-C(31) | 123.40(14) |
| C(29)-C(30)-H(30) | 118.3 |
| C(31)-C(30)-H(30) | 118.3 |
| C(30)-C(31)-C(26) | 119.27(14) |
| C(30)-C(31)-C(34) | 114.95(13) |
| C(26)-C(31)-C(34) | 125.77(14) |
| C(27)-C(32)-H(32A) | 109.5 |
| C(27)-C(32)-H(32B) | 109.5 |
| H(32A)-C(32)-H(32B) | 109.5 |
| C(27)-C(32)-H(32C) | 109.5 |
| H(32A)-C(32)-H(32C) | 109.5 |
| H(32B)-C(32)-H(32C) | 109.5 |
| C(29)-C(33)-H(33A) | 109.5 |
| C(29)-C(33)-H(33B) | 109.5 |
| H(33A)-C(33)-H(33B) | 109.5 |
| C(29)-C(33)-H(33C) | 109.5 |
| H(33A)-C(33)-H(33C) | 109.5 |
| H(33B)-C(33)-H(33C) | 109.5 |
| C(31)-C(34)-H(34A) | 109.5 |
| C(31)-C(34)-H(34B) | 109.5 |
| H(34A)-C(34)-H(34B) | 109.5 |
| C(31)-C(34)-H(34C) | 109.5 |
| H(34A)-C(34)-H(34C) | 109.5 |
| H(34B)-C(34)-H(34C) | 109.5 |

Table C.4n Anisotropic displacement parameters (A^2 x 10^3) for ydbmes. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|

| | | | | | | |
|---|---|---|---|---|---|---|
| O(1) | 23(1) | 26(1) | 26(1) | 13(1) | 3(1) | 9(1) |
| O(2) | 27(1) | 22(1) | 20(1) | 9(1) | 6(1) | 6(1) |
| O(3) | 19(1) | 22(1) | 22(1) | 11(1) | 4(1) | 4(1) |
| O(4) | 28(1) | 31(1) | 22(1) | 13(1) | 7(1) | 15(1) |
| O(5) | 36(1) | 29(1) | 28(1) | 17(1) | 17(1) | 19(1) |
| O(6) | 21(1) | 17(1) | 27(1) | 8(1) | 4(1) | 6(1) |
| C(1) | 20(1) | 17(1) | 23(1) | 12(1) | 5(1) | 5(1) |
| C(2) | 19(1) | 21(1) | 18(1) | 9(1) | 5(1) | 6(1) |
| C(3) | 26(1) | 20(1) | 22(1) | 10(1) | 9(1) | 9(1) |
| C(4) | 31(1) | 23(1) | 28(1) | 14(1) | 13(1) | 15(1) |
| C(5) | 25(1) | 31(1) | 34(1) | 18(1) | 11(1) | 15(1) |
| C(6) | 21(1) | 21(1) | 22(1) | 10(1) | 5(1) | 4(1) |
| C(7) | 33(1) | 22(1) | 22(1) | 8(1) | 8(1) | 8(1) |
| C(8) | 20(1) | 19(1) | 18(1) | 9(1) | 6(1) | 6(1) |
| C(9) | 20(1) | 16(1) | 18(1) | 7(1) | 4(1) | 4(1) |
| C(10) | 23(1) | 17(1) | 22(1) | 9(1) | 7(1) | 7(1) |
| C(11) | 21(1) | 20(1) | 24(1) | 10(1) | 6(1) | 8(1) |
| C(12) | 22(1) | 15(1) | 22(1) | 9(1) | 3(1) | 5(1) |
| C(13) | 23(1) | 19(1) | 19(1) | 8(1) | 5(1) | 5(1) |
| C(14) | 20(1) | 16(1) | 21(1) | 9(1) | 4(1) | 4(1) |
| C(15) | 30(1) | 28(1) | 22(1) | 11(1) | 10(1) | 16(1) |
| C(16) | 24(1) | 25(1) | 25(1) | 12(1) | 2(1) | 9(1) |
| C(17) | 23(1) | 29(1) | 21(1) | 13(1) | 7(1) | 9(1) |
| C(18) | 26(1) | 17(1) | 24(1) | 11(1) | 7(1) | 9(1) |
| C(19) | 19(1) | 20(1) | 21(1) | 10(1) | 6(1) | 8(1) |
| C(20) | 20(1) | 20(1) | 22(1) | 10(1) | 7(1) | 10(1) |
| C(21) | 22(1) | 23(1) | 26(1) | 15(1) | 9(1) | 11(1) |
| C(22) | 23(1) | 33(1) | 26(1) | 17(1) | 8(1) | 13(1) |
| C(23) | 22(1) | 20(1) | 31(1) | 14(1) | 7(1) | 7(1) |
| C(24) | 29(1) | 25(1) | 23(1) | 10(1) | 8(1) | 12(1) |
| C(25) | 16(1) | 17(1) | 21(1) | 9(1) | 4(1) | 5(1) |
| C(26) | 19(1) | 16(1) | 23(1) | 10(1) | 7(1) | 7(1) |
| C(27) | 20(1) | 16(1) | 23(1) | 9(1) | 6(1) | 6(1) |
| C(28) | 20(1) | 20(1) | 25(1) | 11(1) | 4(1) | 7(1) |
| C(29) | 28(1) | 17(1) | 22(1) | 10(1) | 5(1) | 6(1) |
| C(30) | 26(1) | 19(1) | 25(1) | 13(1) | 12(1) | 9(1) |
| C(31) | 21(1) | 18(1) | 26(1) | 12(1) | 8(1) | 8(1) |
| C(32) | 20(1) | 32(1) | 28(1) | 17(1) | 9(1) | 11(1) |
| C(33) | 34(1) | 25(1) | 25(1) | 13(1) | 3(1) | 5(1) |
| C(34) | 21(1) | 33(1) | 35(1) | 23(1) | 10(1) | 9(1) |

Table C.5n Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for ydbmes.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(3) | 4730(30) | 4820(20) | 6190(20) | 57(7) |
| H(6) | 6600(30) | 10530(20) | 4408(18) | 42(6) |
| H(3A) | 5740 | 7253 | 7930 | 26 |
| H(4A) | 5199 | 8797 | 7851 | 30 |
| H(4B) | 6361 | 8679 | 7022 | 30 |
| H(5A) | 3308 | 7028 | 6748 | 33 |
| H(5B) | 3386 | 7814 | 6229 | 33 |
| H(6A) | 9396 | 6929 | 6202 | 32 |
| H(6B) | 9892 | 7548 | 7419 | 32 |
| H(6C) | 9162 | 8113 | 6810 | 32 |
| H(7A) | 8776 | 9033 | 8473 | 40 |
| H(7B) | 8664 | 8146 | 8875 | 40 |
| H(7C) | 7474 | 8939 | 9190 | 40 |
| H(8) | 7211 | 5247 | 6195 | 22 |
| H(11) | 12126 | 5289 | 7869 | 26 |
| H(13) | 9440 | 6277 | 10041 | 25 |
| H(15A) | 11125 | 4809 | 6235 | 38 |
| H(15B) | 9991 | 5504 | 6020 | 38 |
| H(15C) | 9065 | 4302 | 5857 | 38 |
| H(16A) | 13406 | 6598 | 10092 | 37 |
| H(16B) | 12946 | 5295 | 9549 | 37 |
| H(16C) | 12038 | 5895 | 10444 | 37 |
| H(17A) | 6413 | 5984 | 9540 | 35 |
| H(17B) | 5683 | 6065 | 8548 | 35 |
| H(17C) | 6953 | 7129 | 9516 | 35 |
| H(20) | 8066 | 8401 | 3100 | 23 |
| H(21A) | 7397 | 6615 | 3577 | 26 |
| H(21B) | 9127 | 7024 | 3244 | 26 |
| H(22A) | 9650 | 7830 | 5020 | 30 |
| H(22B) | 9798 | 8758 | 4666 | 30 |
| H(23A) | 4326 | 6435 | 3080 | 35 |
| H(23B) | 3580 | 6932 | 2406 | 35 |
| H(23C) | 3230 | 7268 | 3524 | 35 |
| H(24A) | 7670 | 6837 | 1603 | 38 |
| H(24B) | 5950 | 7195 | 1551 | 38 |
| H(24C) | 5960 | 6207 | 1802 | 38 |
| H(25) | 4483 | 9242 | 3896 | 22 |
| H(28) | 1118 | 8502 | 980 | 26 |
| H(30) | 5908 | 9129 | 472 | 26 |
| H(32A) | 534 | 8491 | 2405 | 37 |
| H(32B) | 1969 | 9399 | 3400 | 37 |
| H(32C) | 1807 | 8133 | 2998 | 37 |

| | | | | |
|---|---|---|---|---|
| H(33A) | 3593 | 8759 | -822 | 42 |
| H(33B) | 1920 | 9061 | -447 | 42 |
| H(33C) | 1949 | 7821 | -922 | 42 |
| H(34A) | 8252 | 8892 | 1760 | 40 |
| H(34B) | 8258 | 9832 | 2849 | 40 |
| H(34C) | 8303 | 10081 | 1900 | 40 |

Table C.6n Torsion angles [deg] for ydbmes.

| | |
|---|---|
| C(5)-O(1)-C(1)-O(2) | -171.94(13) |
| C(5)-O(1)-C(1)-C(2) | 10.9(2) |
| O(2)-C(1)-C(2)-C(6) | 50.19(17) |
| O(1)-C(1)-C(2)-C(6) | -132.76(14) |
| O(2)-C(1)-C(2)-C(3) | 172.03(13) |
| O(1)-C(1)-C(2)-C(3) | -10.91(19) |
| O(2)-C(1)-C(2)-C(8) | -66.19(16) |
| O(1)-C(1)-C(2)-C(8) | 110.87(14) |
| C(1)-C(2)-C(3)-C(4) | -24.70(17) |
| C(6)-C(2)-C(3)-C(4) | 93.92(15) |
| C(8)-C(2)-C(3)-C(4) | -139.87(13) |
| C(1)-C(2)-C(3)-C(7) | -149.83(13) |
| C(6)-C(2)-C(3)-C(7) | -31.21(17) |
| C(8)-C(2)-C(3)-C(7) | 95.00(15) |
| C(7)-C(3)-C(4)-C(5) | -172.17(12) |
| C(2)-C(3)-C(4)-C(5) | 60.46(16) |
| C(1)-O(1)-C(5)-C(4) | 25.96(18) |
| C(3)-C(4)-C(5)-O(1) | -62.09(16) |
| C(1)-C(2)-C(8)-O(3) | -69.51(13) |
| C(6)-C(2)-C(8)-O(3) | 178.27(12) |
| C(3)-C(2)-C(8)-O(3) | 52.06(16) |
| C(1)-C(2)-C(8)-C(9) | 162.73(11) |
| C(6)-C(2)-C(8)-C(9) | 50.52(16) |
| C(3)-C(2)-C(8)-C(9) | -75.70(16) |
| O(3)-C(8)-C(9)-C(14) | -40.32(19) |
| C(2)-C(8)-C(9)-C(14) | 85.96(17) |
| O(3)-C(8)-C(9)-C(10) | 136.77(13) |
| C(2)-C(8)-C(9)-C(10) | -96.95(15) |
| C(14)-C(9)-C(10)-C(11) | -5.3(2) |
| C(8)-C(9)-C(10)-C(11) | 177.43(13) |
| C(14)-C(9)-C(10)-C(15) | 171.14(14) |
| C(8)-C(9)-C(10)-C(15) | -6.1(2) |
| C(9)-C(10)-C(11)-C(12) | 2.2(2) |
| C(15)-C(10)-C(11)-C(12) | -174.41(14) |
| C(10)-C(11)-C(12)-C(13) | 1.9(2) |

| | |
|---|---|
| C(10)-C(11)-C(12)-C(16) | -177.54(14) |
| C(11)-C(12)-C(13)-C(14) | -3.0(2) |
| C(16)-C(12)-C(13)-C(14) | 176.43(14) |
| C(12)-C(13)-C(14)-C(9) | -0.1(2) |
| C(12)-C(13)-C(14)-C(17) | 177.78(14) |
| C(10)-C(9)-C(14)-C(13) | 4.2(2) |
| C(8)-C(9)-C(14)-C(13) | -178.71(13) |
| C(10)-C(9)-C(14)-C(17) | -173.41(14) |
| C(8)-C(9)-C(14)-C(17) | 3.6(2) |
| C(22)-O(4)-C(18)-O(5) | 177.62(13) |
| C(22)-O(4)-C(18)-C(19) | -2.1(2) |
| O(5)-C(18)-C(19)-C(23) | -56.81(17) |
| O(4)-C(18)-C(19)-C(23) | 122.86(14) |
| O(5)-C(18)-C(19)-C(20) | -178.97(13) |
| O(4)-C(18)-C(19)-C(20) | 0.70(19) |
| O(5)-C(18)-C(19)-C(25) | 59.27(17) |
| O(4)-C(18)-C(19)-C(25) | -121.06(14) |
| C(18)-C(19)-C(20)-C(24) | 154.87(13) |
| C(23)-C(19)-C(20)-C(24) | 35.86(17) |
| C(25)-C(19)-C(20)-C(24) | -89.84(15) |
| C(18)-C(19)-C(20)-C(21) | 30.53(17) |
| C(23)-C(19)-C(20)-C(21) | -88.48(15) |
| C(25)-C(19)-C(20)-C(21) | 145.82(13) |
| C(24)-C(20)-C(21)-C(22) | 171.77(12) |
| C(19)-C(20)-C(21)-C(22) | -61.39(16) |
| C(18)-O(4)-C(22)-C(21) | -29.01(19) |
| C(20)-C(21)-C(22)-O(4) | 61.01(16) |
| C(18)-C(19)-C(25)-O(6) | 57.39(13) |
| C(23)-C(19)-C(25)-O(6) | 169.60(12) |
| C(20)-C(19)-C(25)-O(6) | -64.51(15) |
| C(18)-C(19)-C(25)-C(26) | -174.45(12) |
| C(23)-C(19)-C(25)-C(26) | -62.23(16) |
| C(20)-C(19)-C(25)-C(26) | 63.65(17) |
| O(6)-C(25)-C(26)-C(31) | 38.92(19) |
| C(19)-C(25)-C(26)-C(31) | -85.53(17) |
| O(6)-C(25)-C(26)-C(27) | -137.52(13) |
| C(19)-C(25)-C(26)-C(27) | 98.03(15) |
| C(31)-C(26)-C(27)-C(28) | 4.8(2) |
| C(25)-C(26)-C(27)-C(28) | -178.53(13) |
| C(31)-C(26)-C(27)-C(32) | -172.84(13) |
| C(25)-C(26)-C(27)-C(32) | 3.9(2) |
| C(26)-C(27)-C(28)-C(29) | -0.5(2) |
| C(32)-C(27)-C(28)-C(29) | 177.20(14) |
| C(27)-C(28)-C(29)-C(30) | -2.7(2) |
| C(27)-C(28)-C(29)-C(33) | 177.19(14) |
| C(28)-C(29)-C(30)-C(31) | 1.6(2) |

| | |
|---|---|
| C(33)-C(29)-C(30)-C(31) | -178.27(14) |
| C(29)-C(30)-C(31)-C(26) | 2.7(2) |
| C(29)-C(30)-C(31)-C(34) | -177.15(14) |
| C(27)-C(26)-C(31)-C(30) | -5.7(2) |
| C(25)-C(26)-C(31)-C(30) | 177.82(13) |
| C(27)-C(26)-C(31)-C(34) | 174.07(14) |
| C(25)-C(26)-C(31)-C(34) | -2.4(2) |

Table C.7n Hydrogen bonds for ydbmes [A and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(3)-H(3)...O(2)#1 | 0.99(3) | 1.73(3) | 2.7167(16) | 170(2) |
| O(6)-H(6)...O(5)#2 | 0.86(2) | 1.95(2) | 2.7658(15) | 156(2) |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1 #2 -x+1,-y+2,-z+1

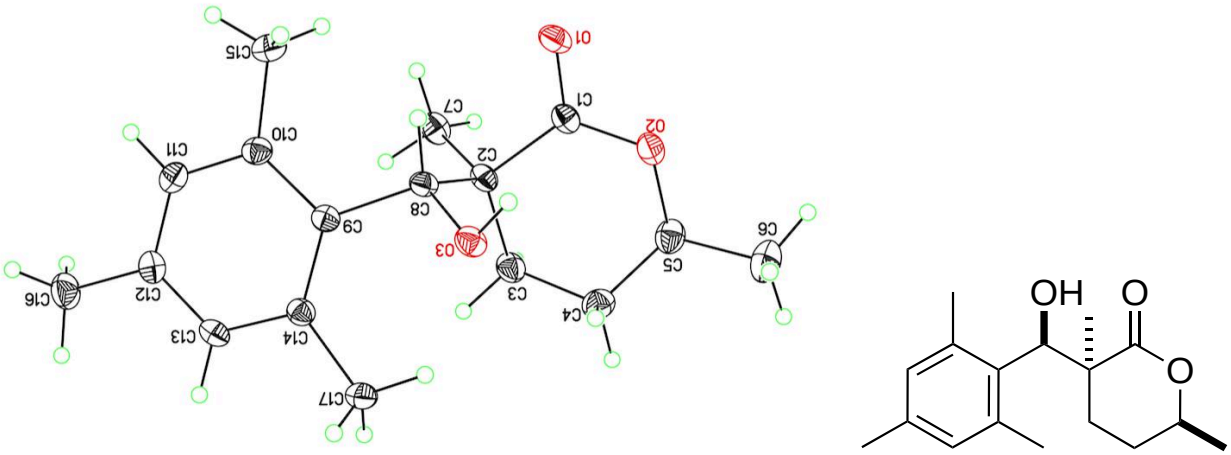



Figure C.15 Structure of yddmes.

**Structure Determination.**

Colorless needles of **yddmes** were grown from a dichloromethane/hexanes solution of the compound at 22 deg. C. A crystal of dimensions 0.11 x 0.11 x 0.09 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (ë = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ù. The exposure times were 1 sec. for the low angle images, 6 sec. for high angle. The integration of the data yielded a total of 43333 reflections to a maximum 2è value of 136.46° of which 2788 were independent and 2536 were greater than

2ó(I). The final cell constants (Table 1) were based on the xyz centroids 25674 reflections above 10ó(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group Pbca with Z = 8 for the formula $C_{17}H_{24}O_3$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in both idealized and refined positions. Full matrix least-squares refinement based on $F^2$ converged at R1 = 0.0379 and wR2 = 0.0943 [based on I > 2sigma(I)], R1 = 0.0411 and wR2 = 0.0965 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.
Sheldrick, G.M. SHELXTL, v. 2014/6; Bruker Analytical X-ray, Madison, WI, 2014.
CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

Table C.1o Crystal data and structure refinement for yddmes.

| | |
|---|---|
| Identification code | yddmes |
| Empirical formula | C17 H24 O3 |
| Formula weight | 276.36 |
| Temperature | 85(2) K |
| Wavelength | 1.54178 A |
| Crystal system, space group | Orthorhombic, Pbca |
| Unit cell dimensions | a = 7.17060(10) A alpha = 90 deg.<br>b = 16.8456(3) A beta = 90 deg.<br>c = 25.1510(18) A gamma = 90 deg. |
| Volume | 3038.1(2) A^3 |
| Z, Calculated density | 8, 1.208 Mg/m^3 |
| Absorption coefficient | 0.647 mm^-1 |
| F(000) | 1200 |
| Crystal size | 0.110 x 0.110 x 0.090 mm |
| Theta range for data collection | 3.514 to 68.230 deg. |
| Limiting indices | -8<=h<=8, -20<=k<=20, -30<=l<=30 |
| Reflections collected / unique | 43333 / 2788 [R(int) = 0.0651] |
| Completeness to theta = 67.679 | 100.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.943 and 0.795 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 2788 / 0 / 191 |
| Goodness-of-fit on F^2 | 1.078 |
| Final R indices [I>2sigma(I)] | R1 = 0.0379, wR2 = 0.0943 |
| R indices (all data) | R1 = 0.0411, wR2 = 0.0965 |
| Extinction coefficient | 0.00143(17) |
| Largest diff. peak and hole | 0.255 and -0.175 e.A^-3 |

Table C.2o Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for yddmes. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 3738(1) | 4206(1) | 5010(1) | 21(1) |
| O(2) | 1999(1) | 5016(1) | 4554(1) | 23(1) |
| O(3) | 6576(1) | 5011(1) | 4033(1) | 19(1) |
| C(1) | 3225(2) | 4426(1) | 4572(1) | 18(1) |
| C(2) | 4011(2) | 4035(1) | 4070(1) | 17(1) |
| C(3) | 3117(2) | 4349(1) | 3557(1) | 22(1) |
| C(4) | 2503(2) | 5206(1) | 3601(1) | 24(1) |
| C(5) | 1143(2) | 5283(1) | 4052(1) | 24(1) |
| C(6) | 486(2) | 6119(1) | 4163(1) | 31(1) |
| C(7) | 3562(2) | 3145(1) | 4114(1) | 22(1) |
| C(8) | 6180(2) | 4188(1) | 4107(1) | 16(1) |
| C(9) | 7320(2) | 3668(1) | 3733(1) | 16(1) |
| C(10) | 8051(2) | 2950(1) | 3940(1) | 18(1) |
| C(11) | 8909(2) | 2408(1) | 3603(1) | 20(1) |
| C(12) | 9149(2) | 2554(1) | 3064(1) | 20(1) |
| C(13) | 8561(2) | 3285(1) | 2873(1) | 20(1) |
| C(14) | 7668(2) | 3848(1) | 3195(1) | 17(1) |
| C(15) | 8071(2) | 2757(1) | 4528(1) | 25(1) |
| C(16) | 10047(2) | 1946(1) | 2707(1) | 28(1) |
| C(17) | 7243(2) | 4638(1) | 2928(1) | 22(1) |

Table C.3o Bond lengths [A] and angles [deg] for yddmes.

| | |
|---|---|
| O(1)-C(1) | 1.2186(15) |
| O(2)-C(1) | 1.3279(16) |
| O(2)-C(5) | 1.4733(16) |
| O(3)-C(8) | 1.4269(14) |
| O(3)-H(3) | 0.89(2) |
| C(1)-C(2) | 1.5319(16) |
| C(2)-C(3) | 1.5346(17) |
| C(2)-C(7) | 1.5366(17) |
| C(2)-C(8) | 1.5799(18) |
| C(3)-C(4) | 1.5137(18) |
| C(3)-H(3A) | 0.9900 |
| C(3)-H(3B) | 0.9900 |
| C(4)-C(5) | 1.5030(19) |
| C(4)-H(4A) | 0.9900 |
| C(4)-H(4B) | 0.9900 |
| C(5)-C(6) | 1.5096(18) |
| C(5)-H(5) | 1.0000 |

| | |
|---|---|
| C(6)-H(6A) | 0.9800 |
| C(6)-H(6B) | 0.9800 |
| C(6)-H(6C) | 0.9800 |
| C(7)-H(7A) | 0.9800 |
| C(7)-H(7B) | 0.9800 |
| C(7)-H(7C) | 0.9800 |
| C(8)-C(9) | 1.5238(16) |
| C(8)-H(8) | 1.0000 |
| C(9)-C(14) | 1.4093(17) |
| C(9)-C(10) | 1.4172(17) |
| C(10)-C(11) | 1.3902(18) |
| C(10)-C(15) | 1.5159(17) |
| C(11)-C(12) | 1.3874(19) |
| C(11)-H(11) | 0.9500 |
| C(12)-C(13) | 1.3867(18) |
| C(12)-C(16) | 1.5079(17) |
| C(13)-C(14) | 1.4024(18) |
| C(13)-H(13) | 0.9500 |
| C(14)-C(17) | 1.5208(17) |
| C(15)-H(15A) | 0.9800 |
| C(15)-H(15B) | 0.9800 |
| C(15)-H(15C) | 0.9800 |
| C(16)-H(16A) | 0.9800 |
| C(16)-H(16B) | 0.9800 |
| C(16)-H(16C) | 0.9800 |
| C(17)-H(17A) | 0.9800 |
| C(17)-H(17B) | 0.9800 |
| C(17)-H(17C) | 0.9800 |
| C(1)-O(2)-C(5) | 122.32(10) |
| C(8)-O(3)-H(3) | 107.6(13) |
| O(1)-C(1)-O(2) | 117.29(11) |
| O(1)-C(1)-C(2) | 120.26(11) |
| O(2)-C(1)-C(2) | 122.43(11) |
| C(1)-C(2)-C(3) | 113.08(10) |
| C(1)-C(2)-C(7) | 106.44(10) |
| C(3)-C(2)-C(7) | 107.97(10) |
| C(1)-C(2)-C(8) | 104.06(10) |
| C(3)-C(2)-C(8) | 113.88(10) |
| C(7)-C(2)-C(8) | 111.17(10) |
| C(4)-C(3)-C(2) | 112.89(10) |
| C(4)-C(3)-H(3A) | 109.0 |
| C(2)-C(3)-H(3A) | 109.0 |
| C(4)-C(3)-H(3B) | 109.0 |
| C(2)-C(3)-H(3B) | 109.0 |
| H(3A)-C(3)-H(3B) | 107.8 |
| C(5)-C(4)-C(3) | 109.04(11) |

| | |
|---|---|
| C(5)-C(4)-H(4A) | 109.9 |
| C(3)-C(4)-H(4A) | 109.9 |
| C(5)-C(4)-H(4B) | 109.9 |
| C(3)-C(4)-H(4B) | 109.9 |
| H(4A)-C(4)-H(4B) | 108.3 |
| O(2)-C(5)-C(4) | 110.52(11) |
| O(2)-C(5)-C(6) | 104.94(11) |
| C(4)-C(5)-C(6) | 114.98(12) |
| O(2)-C(5)-H(5) | 108.7 |
| C(4)-C(5)-H(5) | 108.7 |
| C(6)-C(5)-H(5) | 108.7 |
| C(5)-C(6)-H(6A) | 109.5 |
| C(5)-C(6)-H(6B) | 109.5 |
| H(6A)-C(6)-H(6B) | 109.5 |
| C(5)-C(6)-H(6C) | 109.5 |
| H(6A)-C(6)-H(6C) | 109.5 |
| H(6B)-C(6)-H(6C) | 109.5 |
| C(2)-C(7)-H(7A) | 109.5 |
| C(2)-C(7)-H(7B) | 109.5 |
| H(7A)-C(7)-H(7B) | 109.5 |
| C(2)-C(7)-H(7C) | 109.5 |
| H(7A)-C(7)-H(7C) | 109.5 |
| H(7B)-C(7)-H(7C) | 109.5 |
| O(3)-C(8)-C(9) | 111.76(10) |
| O(3)-C(8)-C(2) | 110.28(10) |
| C(9)-C(8)-C(2) | 113.42(10) |
| O(3)-C(8)-H(8) | 107.0 |
| C(9)-C(8)-H(8) | 107.0 |
| C(2)-C(8)-H(8) | 107.0 |
| C(14)-C(9)-C(10) | 118.08(11) |
| C(14)-C(9)-C(8) | 124.37(11) |
| C(10)-C(9)-C(8) | 117.55(10) |
| C(11)-C(10)-C(9) | 120.07(11) |
| C(11)-C(10)-C(15) | 116.76(11) |
| C(9)-C(10)-C(15) | 123.03(11) |
| C(12)-C(11)-C(10) | 122.22(12) |
| C(12)-C(11)-H(11) | 118.9 |
| C(10)-C(11)-H(11) | 118.9 |
| C(13)-C(12)-C(11) | 117.29(11) |
| C(13)-C(12)-C(16) | 121.77(12) |
| C(11)-C(12)-C(16) | 120.93(12) |
| C(12)-C(13)-C(14) | 122.66(12) |
| C(12)-C(13)-H(13) | 118.7 |
| C(14)-C(13)-H(13) | 118.7 |
| C(13)-C(14)-C(9) | 119.30(11) |
| C(13)-C(14)-C(17) | 115.40(11) |

| | |
|---|---|
| C(9)-C(14)-C(17) | 125.22(11) |
| C(10)-C(15)-H(15A) | 109.5 |
| C(10)-C(15)-H(15B) | 109.5 |
| H(15A)-C(15)-H(15B) | 109.5 |
| C(10)-C(15)-H(15C) | 109.5 |
| H(15A)-C(15)-H(15C) | 109.5 |
| H(15B)-C(15)-H(15C) | 109.5 |
| C(12)-C(16)-H(16A) | 109.5 |
| C(12)-C(16)-H(16B) | 109.5 |
| H(16A)-C(16)-H(16B) | 109.5 |
| C(12)-C(16)-H(16C) | 109.5 |
| H(16A)-C(16)-H(16C) | 109.5 |
| H(16B)-C(16)-H(16C) | 109.5 |
| C(14)-C(17)-H(17A) | 109.5 |
| C(14)-C(17)-H(17B) | 109.5 |
| H(17A)-C(17)-H(17B) | 109.5 |
| C(14)-C(17)-H(17C) | 109.5 |
| H(17A)-C(17)-H(17C) | 109.5 |
| H(17B)-C(17)-H(17C) | 109.5 |

Table C.4o Anisotropic displacement parameters (A^2 x 10^3) for yddmes. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| O(1) | 28(1) | 21(1) | 15(1) | -1(1) | 3(1) | -2(1) |
| O(2) | 24(1) | 26(1) | 20(1) | -3(1) | 2(1) | 6(1) |
| O(3) | 23(1) | 17(1) | 17(1) | -3(1) | 2(1) | -3(1) |
| C(1) | 17(1) | 18(1) | 18(1) | -2(1) | 3(1) | -3(1) |
| C(2) | 18(1) | 20(1) | 14(1) | -3(1) | 1(1) | 0(1) |
| C(3) | 21(1) | 27(1) | 17(1) | -3(1) | -1(1) | 2(1) |
| C(4) | 26(1) | 24(1) | 21(1) | 2(1) | -3(1) | 1(1) |
| C(5) | 21(1) | 24(1) | 26(1) | -3(1) | -4(1) | 3(1) |
| C(6) | 32(1) | 23(1) | 39(1) | -6(1) | -5(1) | 6(1) |
| C(7) | 22(1) | 21(1) | 23(1) | -5(1) | 3(1) | -4(1) |
| C(8) | 18(1) | 17(1) | 12(1) | 0(1) | 1(1) | -1(1) |
| C(9) | 16(1) | 17(1) | 14(1) | -1(1) | -1(1) | -2(1) |
| C(10) | 17(1) | 21(1) | 17(1) | 2(1) | -2(1) | -2(1) |
| C(11) | 18(1) | 18(1) | 23(1) | 2(1) | -2(1) | 1(1) |
| C(12) | 17(1) | 21(1) | 22(1) | -3(1) | 1(1) | 1(1) |
| C(13) | 21(1) | 24(1) | 14(1) | 0(1) | 3(1) | -1(1) |
| C(14) | 17(1) | 19(1) | 15(1) | -1(1) | 0(1) | 0(1) |
| C(15) | 30(1) | 27(1) | 18(1) | 4(1) | -2(1) | 4(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(16) | 29(1) | 25(1) | 29(1) | -5(1) | 5(1) | 5(1) |
| C(17) | 29(1) | 21(1) | 16(1) | 3(1) | 3(1) | 2(1) |

Table C.5o Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for yddmes.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(3) | 6550(30) | 5242(12) | 4352(9) | 47(5) |
| H(3A) | 4026 | 4299 | 3262 | 26 |
| H(3B) | 2022 | 4016 | 3468 | 26 |
| H(4A) | 3599 | 5550 | 3665 | 28 |
| H(4B) | 1906 | 5376 | 3264 | 28 |
| H(5) | 33 | 4943 | 3976 | 28 |
| H(6A) | -357 | 6116 | 4469 | 47 |
| H(6B) | -174 | 6324 | 3851 | 47 |
| H(6C) | 1563 | 6458 | 4240 | 47 |
| H(7A) | 4132 | 2930 | 4437 | 33 |
| H(7B) | 4061 | 2867 | 3802 | 33 |
| H(7C) | 2208 | 3072 | 4129 | 33 |
| H(8) | 6570 | 4050 | 4478 | 19 |
| H(11) | 9347 | 1920 | 3746 | 24 |
| H(13) | 8771 | 3408 | 2509 | 24 |
| H(15A) | 8663 | 2239 | 4583 | 38 |
| H(15B) | 6788 | 2741 | 4663 | 38 |
| H(15C) | 8774 | 3166 | 4720 | 38 |
| H(16A) | 10136 | 2158 | 2345 | 41 |
| H(16B) | 9289 | 1462 | 2704 | 41 |
| H(16C) | 11299 | 1822 | 2839 | 41 |
| H(17A) | 8413 | 4910 | 2843 | 33 |
| H(17B) | 6503 | 4969 | 3169 | 33 |
| H(17C) | 6538 | 4544 | 2600 | 33 |

Table C.6o Torsion angles [deg] for yddmes.

| | |
|---|---|
| C(5)-O(2)-C(1)-O(1) | -174.20(11) |
| C(5)-O(2)-C(1)-C(2) | 6.81(18) |
| O(1)-C(1)-C(2)-C(3) | 176.32(11) |
| O(2)-C(1)-C(2)-C(3) | -4.73(17) |
| O(1)-C(1)-C(2)-C(7) | 57.92(15) |
| O(2)-C(1)-C(2)-C(7) | -123.12(13) |

| | |
|---|---|
| O(1)-C(1)-C(2)-C(8) | -59.60(14) |
| O(2)-C(1)-C(2)-C(8) | 119.36(12) |
| C(1)-C(2)-C(3)-C(4) | 30.65(15) |
| C(7)-C(2)-C(3)-C(4) | 148.15(11) |
| C(8)-C(2)-C(3)-C(4) | -87.87(13) |
| C(2)-C(3)-C(4)-C(5) | -57.97(15) |
| C(1)-O(2)-C(5)-C(4) | -34.08(16) |
| C(1)-O(2)-C(5)-C(6) | -158.60(12) |
| C(3)-C(4)-C(5)-O(2) | 58.29(14) |
| C(3)-C(4)-C(5)-C(6) | 176.86(12) |
| C(1)-C(2)-C(8)-O(3) | -69.41(12) |
| C(3)-C(2)-C(8)-O(3) | 54.15(13) |
| C(7)-C(2)-C(8)-O(3) | 176.39(9) |
| C(1)-C(2)-C(8)-C(9) | 164.38(10) |
| C(3)-C(2)-C(8)-C(9) | -72.06(13) |
| C(7)-C(2)-C(8)-C(9) | 50.18(13) |
| O(3)-C(8)-C(9)-C(14) | -40.86(16) |
| C(2)-C(8)-C(9)-C(14) | 84.56(15) |
| O(3)-C(8)-C(9)-C(10) | 140.18(11) |
| C(2)-C(8)-C(9)-C(10) | -94.40(13) |
| C(14)-C(9)-C(10)-C(11) | -6.67(18) |
| C(8)-C(9)-C(10)-C(11) | 172.36(11) |
| C(14)-C(9)-C(10)-C(15) | 168.90(12) |
| C(8)-C(9)-C(10)-C(15) | -12.08(18) |
| C(9)-C(10)-C(11)-C(12) | 2.46(19) |
| C(15)-C(10)-C(11)-C(12) | -173.38(12) |
| C(10)-C(11)-C(12)-C(13) | 2.52(19) |
| C(10)-C(11)-C(12)-C(16) | -178.60(12) |
| C(11)-C(12)-C(13)-C(14) | -3.24(19) |
| C(16)-C(12)-C(13)-C(14) | 177.88(12) |
| C(12)-C(13)-C(14)-C(9) | -1.03(19) |
| C(12)-C(13)-C(14)-C(17) | 175.93(12) |
| C(10)-C(9)-C(14)-C(13) | 5.94(18) |
| C(8)-C(9)-C(14)-C(13) | -173.01(11) |
| C(10)-C(9)-C(14)-C(17) | -170.69(12) |
| C(8)-C(9)-C(14)-C(17) | 10.4(2) |

Table C.7o Hydrogen bonds for yddmes [A and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(3)-H(3)...O(1)#1 | 0.89(2) | 1.87(2) | 2.7538(12) | 173.2(19) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

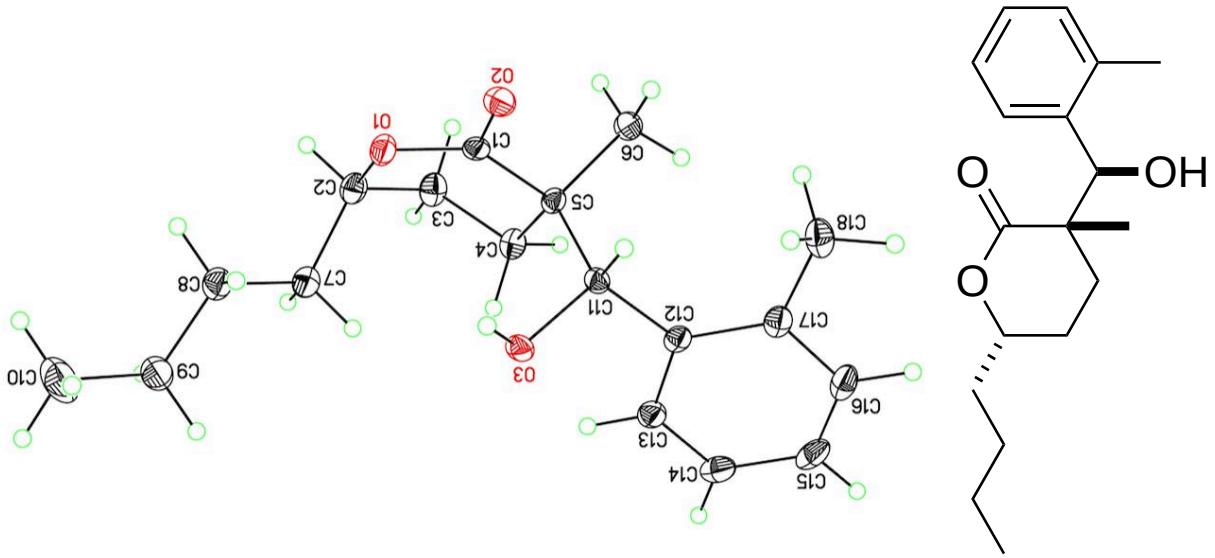



Figure C.16 Structure of yd2memain.

**Structure Determination.**

Colorless block-like crystals of **yd2memain** were grown from a hexanes/ethyl acetate solution of the compound at 22 deg. C. A crystal of dimensions 0.18 x 0.18 x 0.10 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (ë = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ù. The exposure times were 1 sec. for the low angle images, 6 sec. for high angle. The integration of the data yielded a total of 24743 reflections to a maximum 2è value of 136.48° of which 2957 were independent and 2856 were greater than 2ó(I). The final cell constants (Table 1) were based on the xyz centroids 18129 reflections above 10ó(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group C2/c with Z = 8 for the formula $C_{18}H_{26}O_3$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in both idealized and refined positions. Full matrix least-squares refinement based on $F^2$ converged at R1 = 0.0380 and wR2 = 0.0913 [based on I > 2sigma(I)], R1 = 0.0388 and wR2 = 0.0920 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Sheldrick, G.M. SHELXTL, v. 2014/6; Bruker Analytical X-ray, Madison, WI, 2014.
CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

Table C.1p Crystal data and structure refinement for yd2memain.

| | |
|---|---|
| Identification code | yd2memain |
| Empirical formula | C18 H26 O3 |

| | |
|---|---|
| Formula weight | 290.39 |
| Temperature | 85(2) K |
| Wavelength | 1.54178 A |
| Crystal system, space group | Monoclinic, C2/c |
| Unit cell dimensions | a = 17.8182(3) A alpha = 90 deg. |
| | b = 13.4155(3) A beta = 111.749(8) deg. |
| | c = 14.5772(10) A gamma = 90 deg. |
| Volume | 3236.5(3) A^3 |
| Z, Calculated density | 8, 1.192 Mg/m^3 |
| Absorption coefficient | 0.630 mm^-1 |
| F(000) | 1264 |
| Crystal size | 0.180 x 0.180 x 0.100 mm |
| Theta range for data collection | 4.712 to 68.236 deg. |
| Limiting indices | -21<=h<=21, -16<=k<=16, -15<=l<=17 |
| Reflections collected / unique | 24743 / 2957 [R(int) = 0.0616] |
| Completeness to theta = 67.679 | 99.6 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.939 and 0.799 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 2957 / 0 / 198 |
| Goodness-of-fit on F^2 | 1.030 |
| Final R indices [I>2sigma(I)] | R1 = 0.0380, wR2 = 0.0913 |
| R indices (all data) | R1 = 0.0388, wR2 = 0.0920 |
| Extinction coefficient | 0.0026(2) |
| Largest diff. peak and hole | 0.292 and -0.234 e.A^-3 |

Table C.2p Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for yd2memain. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 4499(1) | 4703(1) | 6284(1) | 18(1) |
| O(2) | 5030(1) | 5884(1) | 5696(1) | 17(1) |
| O(3) | 3484(1) | 4924(1) | 3826(1) | 16(1) |
| C(1) | 4418(1) | 5528(1) | 5750(1) | 14(1) |
| C(2) | 3830(1) | 4269(1) | 6516(1) | 18(1) |
| C(3) | 3192(1) | 5050(1) | 6413(1) | 20(1) |
| C(4) | 2899(1) | 5509(1) | 5387(1) | 16(1) |
| C(5) | 3599(1) | 6024(1) | 5198(1) | 13(1) |
| C(6) | 3681(1) | 7113(1) | 5544(1) | 17(1) |
| C(7) | 3522(1) | 3340(1) | 5894(1) | 19(1) |
| C(8) | 4162(1) | 2540(1) | 6011(1) | 20(1) |
| C(9) | 3789(1) | 1538(1) | 5597(1) | 23(1) |

| | | | | |
|---|---|---|---|---|
| C(10) | 4411(1) | 723(1) | 5710(1) | 40(1) |
| C(11) | 3500(1) | 5950(1) | 4086(1) | 13(1) |
| C(12) | 2739(1) | 6432(1) | 3360(1) | 14(1) |
| C(13) | 2021(1) | 5881(1) | 3022(1) | 17(1) |
| C(14) | 1319(1) | 6256(1) | 2316(1) | 22(1) |
| C(15) | 1326(1) | 7193(1) | 1919(1) | 23(1) |
| C(16) | 2034(1) | 7741(1) | 2235(1) | 21(1) |
| C(17) | 2746(1) | 7383(1) | 2956(1) | 17(1) |
| C(18) | 3493(1) | 8027(1) | 3241(1) | 23(1) |

Table C.3p Bond lengths [A] and angles [deg] for yd2memain.

| | |
|---|---|
| O(1)-C(1) | 1.3302(13) |
| O(1)-C(2) | 1.4739(14) |
| O(2)-C(1) | 1.2187(14) |
| O(3)-C(11) | 1.4249(12) |
| O(3)-H(3) | 0.90(2) |
| C(1)-C(5) | 1.5335(14) |
| C(2)-C(3) | 1.5126(16) |
| C(2)-C(7) | 1.5183(16) |
| C(2)-H(2) | 1.0000 |
| C(3)-C(4) | 1.5193(16) |
| C(3)-H(3A) | 0.9900 |
| C(3)-H(3B) | 0.9900 |
| C(4)-C(5) | 1.5372(15) |
| C(4)-H(4A) | 0.9900 |
| C(4)-H(4B) | 0.9900 |
| C(5)-C(6) | 1.5353(15) |
| C(5)-C(11) | 1.5672(14) |
| C(6)-H(6A) | 0.9800 |
| C(6)-H(6B) | 0.9800 |
| C(6)-H(6C) | 0.9800 |
| C(7)-C(8) | 1.5279(15) |
| C(7)-H(7A) | 0.9900 |
| C(7)-H(7B) | 0.9900 |
| C(8)-C(9) | 1.5209(16) |
| C(8)-H(8A) | 0.9900 |
| C(8)-H(8B) | 0.9900 |
| C(9)-C(10) | 1.5212(18) |
| C(9)-H(9A) | 0.9900 |
| C(9)-H(9B) | 0.9900 |
| C(10)-H(10A) | 0.9800 |
| C(10)-H(10B) | 0.9800 |
| C(10)-H(10C) | 0.9800 |

| | |
|---|---|
| C(11)-C(12) | 1.5212(15) |
| C(11)-H(11) | 1.0000 |
| C(12)-C(13) | 1.3995(16) |
| C(12)-C(17) | 1.4067(16) |
| C(13)-C(14) | 1.3866(16) |
| C(13)-H(13) | 0.9500 |
| C(14)-C(15) | 1.3863(18) |
| C(14)-H(14) | 0.9500 |
| C(15)-C(16) | 1.3829(18) |
| C(15)-H(15) | 0.9500 |
| C(16)-C(17) | 1.3994(17) |
| C(16)-H(16) | 0.9500 |
| C(17)-C(18) | 1.5102(17) |
| C(18)-H(18A) | 0.9800 |
| C(18)-H(18B) | 0.9800 |
| C(18)-H(18C) | 0.9800 |
| C(1)-O(1)-C(2) | 122.79(8) |
| C(11)-O(3)-H(3) | 108.2(11) |
| O(2)-C(1)-O(1) | 117.36(9) |
| O(2)-C(1)-C(5) | 119.67(10) |
| O(1)-C(1)-C(5) | 122.96(9) |
| O(1)-C(2)-C(3) | 110.19(9) |
| O(1)-C(2)-C(7) | 109.36(9) |
| C(3)-C(2)-C(7) | 114.73(10) |
| O(1)-C(2)-H(2) | 107.4 |
| C(3)-C(2)-H(2) | 107.4 |
| C(7)-C(2)-H(2) | 107.4 |
| C(2)-C(3)-C(4) | 110.45(9) |
| C(2)-C(3)-H(3A) | 109.6 |
| C(4)-C(3)-H(3A) | 109.6 |
| C(2)-C(3)-H(3B) | 109.6 |
| C(4)-C(3)-H(3B) | 109.6 |
| H(3A)-C(3)-H(3B) | 108.1 |
| C(3)-C(4)-C(5) | 110.69(9) |
| C(3)-C(4)-H(4A) | 109.5 |
| C(5)-C(4)-H(4A) | 109.5 |
| C(3)-C(4)-H(4B) | 109.5 |
| C(5)-C(4)-H(4B) | 109.5 |
| H(4A)-C(4)-H(4B) | 108.1 |
| C(1)-C(5)-C(6) | 106.54(8) |
| C(1)-C(5)-C(4) | 112.84(9) |
| C(6)-C(5)-C(4) | 110.71(9) |
| C(1)-C(5)-C(11) | 103.63(8) |
| C(6)-C(5)-C(11) | 111.13(9) |
| C(4)-C(5)-C(11) | 111.69(9) |
| C(5)-C(6)-H(6A) | 109.5 |

| | |
|---|---|
| C(5)-C(6)-H(6B) | 109.5 |
| H(6A)-C(6)-H(6B) | 109.5 |
| C(5)-C(6)-H(6C) | 109.5 |
| H(6A)-C(6)-H(6C) | 109.5 |
| H(6B)-C(6)-H(6C) | 109.5 |
| C(2)-C(7)-C(8) | 114.87(10) |
| C(2)-C(7)-H(7A) | 108.5 |
| C(8)-C(7)-H(7A) | 108.5 |
| C(2)-C(7)-H(7B) | 108.5 |
| C(8)-C(7)-H(7B) | 108.5 |
| H(7A)-C(7)-H(7B) | 107.5 |
| C(9)-C(8)-C(7) | 112.26(10) |
| C(9)-C(8)-H(8A) | 109.2 |
| C(7)-C(8)-H(8A) | 109.2 |
| C(9)-C(8)-H(8B) | 109.2 |
| C(7)-C(8)-H(8B) | 109.2 |
| H(8A)-C(8)-H(8B) | 107.9 |
| C(8)-C(9)-C(10) | 113.55(10) |
| C(8)-C(9)-H(9A) | 108.9 |
| C(10)-C(9)-H(9A) | 108.9 |
| C(8)-C(9)-H(9B) | 108.9 |
| C(10)-C(9)-H(9B) | 108.9 |
| H(9A)-C(9)-H(9B) | 107.7 |
| C(9)-C(10)-H(10A) | 109.5 |
| C(9)-C(10)-H(10B) | 109.5 |
| H(10A)-C(10)-H(10B) | 109.5 |
| C(9)-C(10)-H(10C) | 109.5 |
| H(10A)-C(10)-H(10C) | 109.5 |
| H(10B)-C(10)-H(10C) | 109.5 |
| O(3)-C(11)-C(12) | 107.50(8) |
| O(3)-C(11)-C(5) | 108.59(8) |
| C(12)-C(11)-C(5) | 114.96(8) |
| O(3)-C(11)-H(11) | 108.5 |
| C(12)-C(11)-H(11) | 108.5 |
| C(5)-C(11)-H(11) | 108.5 |
| C(13)-C(12)-C(17) | 118.70(10) |
| C(13)-C(12)-C(11) | 118.91(10) |
| C(17)-C(12)-C(11) | 122.18(10) |
| C(14)-C(13)-C(12) | 121.68(11) |
| C(14)-C(13)-H(13) | 119.2 |
| C(12)-C(13)-H(13) | 119.2 |
| C(15)-C(14)-C(13) | 119.57(11) |
| C(15)-C(14)-H(14) | 120.2 |
| C(13)-C(14)-H(14) | 120.2 |
| C(16)-C(15)-C(14) | 119.45(11) |
| C(16)-C(15)-H(15) | 120.3 |

| | |
|---|---|
| C(14)-C(15)-H(15) | 120.3 |
| C(15)-C(16)-C(17) | 121.89(11) |
| C(15)-C(16)-H(16) | 119.1 |
| C(17)-C(16)-H(16) | 119.1 |
| C(16)-C(17)-C(12) | 118.69(11) |
| C(16)-C(17)-C(18) | 118.10(10) |
| C(12)-C(17)-C(18) | 123.19(10) |
| C(17)-C(18)-H(18A) | 109.5 |
| C(17)-C(18)-H(18B) | 109.5 |
| H(18A)-C(18)-H(18B) | 109.5 |
| C(17)-C(18)-H(18C) | 109.5 |
| H(18A)-C(18)-H(18C) | 109.5 |
| H(18B)-C(18)-H(18C) | 109.5 |

Table C.4p Anisotropic displacement parameters (A^2 x 10^3) for yd2memain. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| O(1) | 16(1) | 17(1) | 18(1) | 4(1) | 4(1) | 3(1) |
| O(2) | 13(1) | 16(1) | 20(1) | -3(1) | 5(1) | 1(1) |
| O(3) | 15(1) | 13(1) | 17(1) | -4(1) | 4(1) | 2(1) |
| C(1) | 16(1) | 13(1) | 10(1) | -4(1) | 4(1) | 1(1) |
| C(2) | 21(1) | 19(1) | 15(1) | 4(1) | 8(1) | 1(1) |
| C(3) | 24(1) | 21(1) | 18(1) | 3(1) | 12(1) | 4(1) |
| C(4) | 15(1) | 18(1) | 18(1) | 2(1) | 8(1) | 3(1) |
| C(5) | 14(1) | 13(1) | 12(1) | 0(1) | 4(1) | 3(1) |
| C(6) | 19(1) | 15(1) | 17(1) | -2(1) | 6(1) | 3(1) |
| C(7) | 18(1) | 19(1) | 19(1) | 2(1) | 6(1) | 1(1) |
| C(8) | 18(1) | 19(1) | 21(1) | 2(1) | 6(1) | 2(1) |
| C(9) | 22(1) | 20(1) | 26(1) | -1(1) | 9(1) | 0(1) |
| C(10) | 34(1) | 22(1) | 58(1) | -8(1) | 12(1) | 4(1) |
| C(11) | 15(1) | 11(1) | 13(1) | -1(1) | 6(1) | 1(1) |
| C(12) | 17(1) | 16(1) | 11(1) | -1(1) | 6(1) | 3(1) |
| C(13) | 19(1) | 17(1) | 15(1) | -2(1) | 5(1) | 2(1) |
| C(14) | 18(1) | 26(1) | 17(1) | -5(1) | 2(1) | 3(1) |
| C(15) | 23(1) | 28(1) | 13(1) | 0(1) | 2(1) | 13(1) |
| C(16) | 30(1) | 19(1) | 15(1) | 4(1) | 11(1) | 10(1) |
| C(17) | 22(1) | 17(1) | 14(1) | 0(1) | 9(1) | 4(1) |
| C(18) | 29(1) | 18(1) | 24(1) | 5(1) | 13(1) | 0(1) |

Table C.5p Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for yd2memain.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(3) | 3996(12) | 4720(13) | 3977(13) | 40(5) |
| H(2) | 4055 | 4056 | 7223 | 22 |
| H(3A) | 3420 | 5578 | 6914 | 24 |
| H(3B) | 2731 | 4742 | 6530 | 24 |
| H(4A) | 2469 | 6002 | 5324 | 20 |
| H(4B) | 2667 | 4982 | 4886 | 20 |
| H(6A) | 3720 | 7140 | 6232 | 26 |
| H(6B) | 3207 | 7491 | 5127 | 26 |
| H(6C) | 4169 | 7404 | 5494 | 26 |
| H(7A) | 3286 | 3538 | 5191 | 22 |
| H(7B) | 3084 | 3045 | 6070 | 22 |
| H(8A) | 4519 | 2758 | 5667 | 24 |
| H(8B) | 4498 | 2462 | 6721 | 24 |
| H(9A) | 3455 | 1619 | 4887 | 28 |
| H(9B) | 3427 | 1327 | 5938 | 28 |
| H(10A) | 4745 | 901 | 5332 | 60 |
| H(10B) | 4133 | 91 | 5463 | 60 |
| H(10C) | 4754 | 650 | 6409 | 60 |
| H(11) | 3980 | 6270 | 4008 | 15 |
| H(13) | 2015 | 5234 | 3283 | 21 |
| H(14) | 837 | 5872 | 2105 | 26 |
| H(15) | 849 | 7457 | 1435 | 27 |
| H(16) | 2036 | 8380 | 1954 | 25 |
| H(18A) | 3380 | 8614 | 2811 | 34 |
| H(18B) | 3936 | 7645 | 3168 | 34 |
| H(18C) | 3647 | 8241 | 3929 | 34 |

Table C.6p Torsion angles [deg] for yd2memain.

| | |
|---|---|
| C(2)-O(1)-C(1)-O(2) | 171.94(9) |
| C(2)-O(1)-C(1)-C(5) | -9.07(15) |
| C(1)-O(1)-C(2)-C(3) | -21.12(14) |
| C(1)-O(1)-C(2)-C(7) | 105.86(11) |
| O(1)-C(2)-C(3)-C(4) | 55.84(12) |
| C(7)-C(2)-C(3)-C(4) | -68.09(13) |
| C(2)-C(3)-C(4)-C(5) | -61.12(12) |
| O(2)-C(1)-C(5)-C(6) | -55.46(12) |

| | |
|---|---|
| O(1)-C(1)-C(5)-C(6) | 125.57(10) |
| O(2)-C(1)-C(5)-C(4) | -177.15(10) |
| O(1)-C(1)-C(5)-C(4) | 3.87(14) |
| O(2)-C(1)-C(5)-C(11) | 61.86(12) |
| O(1)-C(1)-C(5)-C(11) | -117.11(10) |
| C(3)-C(4)-C(5)-C(1) | 30.58(12) |
| C(3)-C(4)-C(5)-C(6) | -88.73(11) |
| C(3)-C(4)-C(5)-C(11) | 146.86(9) |
| O(1)-C(2)-C(7)-C(8) | 56.76(12) |
| C(3)-C(2)-C(7)-C(8) | -178.87(10) |
| C(2)-C(7)-C(8)-C(9) | 164.83(10) |
| C(7)-C(8)-C(9)-C(10) | -179.51(11) |
| C(1)-C(5)-C(11)-O(3) | 61.92(10) |
| C(6)-C(5)-C(11)-O(3) | 175.99(8) |
| C(4)-C(5)-C(11)-O(3) | -59.83(11) |
| C(1)-C(5)-C(11)-C(12) | -177.65(9) |
| C(6)-C(5)-C(11)-C(12) | -63.58(12) |
| C(4)-C(5)-C(11)-C(12) | 60.60(12) |
| O(3)-C(11)-C(12)-C(13) | 36.01(13) |
| C(5)-C(11)-C(12)-C(13) | -85.02(12) |
| O(3)-C(11)-C(12)-C(17) | -138.77(10) |
| C(5)-C(11)-C(12)-C(17) | 100.21(12) |
| C(17)-C(12)-C(13)-C(14) | -1.09(16) |
| C(11)-C(12)-C(13)-C(14) | -176.05(10) |
| C(12)-C(13)-C(14)-C(15) | 1.00(17) |
| C(13)-C(14)-C(15)-C(16) | -0.03(17) |
| C(14)-C(15)-C(16)-C(17) | -0.83(17) |
| C(15)-C(16)-C(17)-C(12) | 0.72(17) |
| C(15)-C(16)-C(17)-C(18) | 178.96(10) |
| C(13)-C(12)-C(17)-C(16) | 0.23(15) |
| C(11)-C(12)-C(17)-C(16) | 175.02(10) |
| C(13)-C(12)-C(17)-C(18) | -177.91(10) |
| C(11)-C(12)-C(17)-C(18) | -3.12(16) |

Table C.7p Hydrogen bonds for yd2memain [A and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(3)-H(3)...O(2)#1 | 0.90(2) | 1.81(2) | 2.7039(11) | 171.0(16) |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1

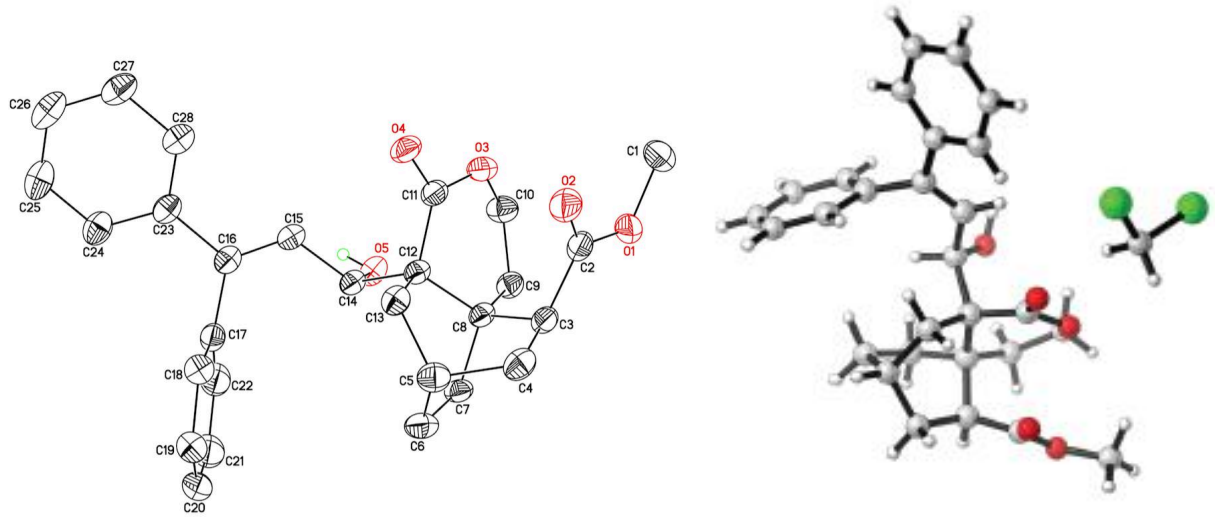



Figure C.17 Structure of yddiph.

**Structure Determination.**

Fine, colorless needles of **yddiph** were grown from a dichloromethane/hexane solution of the compound at -70 deg. C. A crystal of dimensions 0.16 x 0.01 x 0.01 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (ë = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ù. The exposure times were 5 sec. for the low angle images, 40 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 76631 reflections to a maximum 2è value of 140.16° of which 4888 were independent and 4093 were greater than 2ó(I). The final cell constants (Table 1) were based on the xyz centroids 18727 reflections above 10ó(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group Pbca with Z = 8 for the formula $C_{29}H_{32}O_5Cl_2$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in a combination of idealized and refined positions. Full matrix least-squares refinement based on $F^2$ converged at R1 = 0.0551 and wR2 = 0.1486 [based on I > 2sigma(I)], R1 = 0.0648 and wR2 = 0.1600 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Sheldrick, G.M. SHELXTL, v. 2014/6; Bruker Analytical X-ray, Madison, WI, 2014.
CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.
CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015).

Table C.1q Crystal data and structure refinement for yddiph.

| | |
|---|---|
| Identification code | yddiph |
| Empirical formula | C29 H32 Cl2 O5 |

| | |
|---|---|
| Formula weight | 531.44 |
| Temperature | 85(2) K |
| Wavelength | 1.54184 A |
| Crystal system, space group | Orthorhombic, Pbca |
| Unit cell dimensions | a = 21.1760(3) A alpha = 90 deg. |
| | b = 11.5887(2) A beta = 90 deg. |
| | c = 21.3355(5) A gamma = 90 deg. |
| Volume | 5235.80(17) A^3 |
| Z, Calculated density | 8, 1.348 Mg/m^3 |
| Absorption coefficient | 2.541 mm^-1 |
| F(000) | 2240 |
| Crystal size | 0.160 x 0.010 x 0.010 mm |
| Theta range for data collection | 4.144 to 70.080 deg. |
| Limiting indices | -25<=h<=25, -14<=k<=13, -26<=l<=25 |
| Reflections collected / unique | 76631 / 4888 [R(int) = 0.0902] |
| Completeness to theta = 67.684 | 100.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00000 and 0.77082 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 4888 / 0 / 330 |
| Goodness-of-fit on F^2 | 1.073 |
| Final R indices [I>2sigma(I)] | R1 = 0.0551, wR2 = 0.1486 |
| R indices (all data) | R1 = 0.0648, wR2 = 0.1600 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.442 and -0.580 e.A^-3 |

Table C.2q Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for yddiph. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Cl(1) | 5411(1) | 4589(1) | 6206(1) | 72(1) |
| Cl(2) | 5446(1) | 3485(1) | 4978(1) | 64(1) |
| O(1) | 8630(1) | 5667(2) | 4339(1) | 36(1) |
| O(2) | 8158(1) | 6417(2) | 5192(1) | 38(1) |
| O(3) | 7706(1) | 3916(2) | 4892(1) | 33(1) |
| O(4) | 7267(1) | 4483(1) | 5769(1) | 33(1) |
| O(5) | 8276(1) | 1686(1) | 5642(1) | 31(1) |
| C(1) | 8130(1) | 6157(3) | 3961(1) | 46(1) |
| C(2) | 8568(1) | 5829(2) | 4961(1) | 31(1) |
| C(3) | 9072(1) | 5177(2) | 5322(1) | 28(1) |
| C(4) | 9240(1) | 5788(2) | 5942(1) | 34(1) |
| C(5) | 9101(1) | 4983(2) | 6491(1) | 32(1) |
| C(6) | 9548(1) | 3954(2) | 6456(1) | 34(1) |

| | | | | |
|---|---|---|---|---|
| C(7) | 9494(1) | 3394(2) | 5798(1) | 28(1) |
| C(8) | 8915(1) | 3868(2) | 5440(1) | 25(1) |
| C(9) | 8840(1) | 3238(2) | 4809(1) | 30(1) |
| C(10) | 8160(1) | 3181(2) | 4564(1) | 35(1) |
| C(11) | 7728(1) | 4065(2) | 5513(1) | 27(1) |
| C(12) | 8323(1) | 3756(2) | 5870(1) | 24(1) |
| C(13) | 8410(1) | 4590(2) | 6437(1) | 27(1) |
| C(14) | 8244(1) | 2507(2) | 6140(1) | 25(1) |
| C(15) | 7644(1) | 2354(2) | 6510(1) | 26(1) |
| C(16) | 7614(1) | 2168(2) | 7128(1) | 26(1) |
| C(17) | 8198(1) | 2073(2) | 7518(1) | 30(1) |
| C(18) | 8351(1) | 2944(2) | 7941(1) | 34(1) |
| C(19) | 8924(1) | 2930(3) | 8262(1) | 45(1) |
| C(20) | 9340(1) | 2030(3) | 8169(1) | 51(1) |
| C(21) | 9188(1) | 1144(3) | 7769(2) | 53(1) |
| C(22) | 8617(1) | 1154(2) | 7440(1) | 41(1) |
| C(23) | 6995(1) | 2067(2) | 7460(1) | 28(1) |
| C(24) | 6930(1) | 1324(2) | 7971(1) | 35(1) |
| C(25) | 6351(1) | 1215(2) | 8277(1) | 42(1) |
| C(26) | 5836(1) | 1853(2) | 8080(1) | 42(1) |
| C(27) | 5897(1) | 2601(2) | 7578(1) | 37(1) |
| C(28) | 6472(1) | 2713(2) | 7268(1) | 31(1) |
| C(29) | 5814(1) | 4469(3) | 5490(2) | 54(1) |

Table C.3q Bond lengths [A] and angles [deg] for yddiph.

| | |
|---|---|
| Cl(1)-C(29) | 1.755(3) |
| Cl(2)-C(29) | 1.762(3) |
| O(1)-C(2) | 1.347(3) |
| O(1)-C(1) | 1.448(3) |
| O(2)-C(2) | 1.208(3) |
| O(3)-C(11) | 1.336(3) |
| O(3)-C(10) | 1.463(3) |
| O(4)-C(11) | 1.218(3) |
| O(5)-C(14) | 1.428(3) |
| O(5)-H(5) | 0.83(4) |
| C(1)-H(1A) | 0.9800 |
| C(1)-H(1B) | 0.9800 |
| C(1)-H(1C) | 0.9800 |
| C(2)-C(3) | 1.516(3) |
| C(3)-C(4) | 1.544(3) |
| C(3)-C(8) | 1.573(3) |
| C(3)-H(3) | 1.0000 |
| C(4)-C(5) | 1.525(3) |

| | |
|---|---|
| C(4)-H(4A) | 0.9900 |
| C(4)-H(4B) | 0.9900 |
| C(5)-C(6) | 1.524(3) |
| C(5)-C(13) | 1.538(3) |
| C(5)-H(5A) | 1.0000 |
| C(6)-C(7) | 1.551(3) |
| C(6)-H(6A) | 0.9900 |
| C(6)-H(6B) | 0.9900 |
| C(7)-C(8) | 1.545(3) |
| C(7)-H(7A) | 0.9900 |
| C(7)-H(7B) | 0.9900 |
| C(8)-C(9) | 1.539(3) |
| C(8)-C(12) | 1.559(3) |
| C(9)-C(10) | 1.531(3) |
| C(9)-H(9A) | 0.9900 |
| C(9)-H(9B) | 0.9900 |
| C(10)-H(10A) | 0.9900 |
| C(10)-H(10B) | 0.9900 |
| C(11)-C(12) | 1.516(3) |
| C(12)-C(13) | 1.560(3) |
| C(12)-C(14) | 1.566(3) |
| C(13)-H(13A) | 0.9900 |
| C(13)-H(13B) | 0.9900 |
| C(14)-C(15) | 1.506(3) |
| C(14)-H(14) | 1.0000 |
| C(15)-C(16) | 1.338(3) |
| C(15)-H(15) | 0.9500 |
| C(16)-C(23) | 1.494(3) |
| C(16)-C(17) | 1.495(3) |
| C(17)-C(18) | 1.392(4) |
| C(17)-C(22) | 1.395(3) |
| C(18)-C(19) | 1.395(3) |
| C(18)-H(18) | 0.9500 |
| C(19)-C(20) | 1.380(4) |
| C(19)-H(19) | 0.9500 |
| C(20)-C(21) | 1.374(5) |
| C(20)-H(20) | 0.9500 |
| C(21)-C(22) | 1.398(4) |
| C(21)-H(21) | 0.9500 |
| C(22)-H(22) | 0.9500 |
| C(23)-C(24) | 1.396(3) |
| C(23)-C(28) | 1.399(3) |
| C(24)-C(25) | 1.395(3) |
| C(24)-H(24) | 0.9500 |
| C(25)-C(26) | 1.381(4) |
| C(25)-H(25) | 0.9500 |

| | |
|---|---|
| C(26)-C(27) | 1.385(4) |
| C(26)-H(26) | 0.9500 |
| C(27)-C(28) | 1.392(3) |
| C(27)-H(27) | 0.9500 |
| C(28)-H(28) | 0.9500 |
| C(29)-H(29A) | 0.9900 |
| C(29)-H(29B) | 0.9900 |
| C(2)-O(1)-C(1) | 114.96(19) |
| C(11)-O(3)-C(10) | 121.83(17) |
| C(14)-O(5)-H(5) | 111(3) |
| O(1)-C(1)-H(1A) | 109.5 |
| O(1)-C(1)-H(1B) | 109.5 |
| H(1A)-C(1)-H(1B) | 109.5 |
| O(1)-C(1)-H(1C) | 109.5 |
| H(1A)-C(1)-H(1C) | 109.5 |
| H(1B)-C(1)-H(1C) | 109.5 |
| O(2)-C(2)-O(1) | 123.4(2) |
| O(2)-C(2)-C(3) | 125.5(2) |
| O(1)-C(2)-C(3) | 111.14(19) |
| C(2)-C(3)-C(4) | 111.67(19) |
| C(2)-C(3)-C(8) | 114.43(17) |
| C(4)-C(3)-C(8) | 110.70(18) |
| C(2)-C(3)-H(3) | 106.5 |
| C(4)-C(3)-H(3) | 106.5 |
| C(8)-C(3)-H(3) | 106.5 |
| C(5)-C(4)-C(3) | 109.46(18) |
| C(5)-C(4)-H(4A) | 109.8 |
| C(3)-C(4)-H(4A) | 109.8 |
| C(5)-C(4)-H(4B) | 109.8 |
| C(3)-C(4)-H(4B) | 109.8 |
| H(4A)-C(4)-H(4B) | 108.2 |
| C(6)-C(5)-C(4) | 108.7(2) |
| C(6)-C(5)-C(13) | 110.84(18) |
| C(4)-C(5)-C(13) | 107.94(18) |
| C(6)-C(5)-H(5A) | 109.8 |
| C(4)-C(5)-H(5A) | 109.8 |
| C(13)-C(5)-H(5A) | 109.8 |
| C(5)-C(6)-C(7) | 109.02(19) |
| C(5)-C(6)-H(6A) | 109.9 |
| C(7)-C(6)-H(6A) | 109.9 |
| C(5)-C(6)-H(6B) | 109.9 |
| C(7)-C(6)-H(6B) | 109.9 |
| H(6A)-C(6)-H(6B) | 108.3 |
| C(8)-C(7)-C(6) | 110.93(17) |
| C(8)-C(7)-H(7A) | 109.5 |
| C(6)-C(7)-H(7A) | 109.5 |

| | |
|---|---|
| C(8)-C(7)-H(7B) | 109.5 |
| C(6)-C(7)-H(7B) | 109.5 |
| H(7A)-C(7)-H(7B) | 108.0 |
| C(9)-C(8)-C(7) | 110.23(17) |
| C(9)-C(8)-C(12) | 112.99(17) |
| C(7)-C(8)-C(12) | 108.49(17) |
| C(9)-C(8)-C(3) | 109.88(18) |
| C(7)-C(8)-C(3) | 104.81(16) |
| C(12)-C(8)-C(3) | 110.12(16) |
| C(10)-C(9)-C(8) | 114.63(18) |
| C(10)-C(9)-H(9A) | 108.6 |
| C(8)-C(9)-H(9A) | 108.6 |
| C(10)-C(9)-H(9B) | 108.6 |
| C(8)-C(9)-H(9B) | 108.6 |
| H(9A)-C(9)-H(9B) | 107.6 |
| O(3)-C(10)-C(9) | 115.41(19) |
| O(3)-C(10)-H(10A) | 108.4 |
| C(9)-C(10)-H(10A) | 108.4 |
| O(3)-C(10)-H(10B) | 108.4 |
| C(9)-C(10)-H(10B) | 108.4 |
| H(10A)-C(10)-H(10B) | 107.5 |
| O(4)-C(11)-O(3) | 117.97(19) |
| O(4)-C(11)-C(12) | 122.3(2) |
| O(3)-C(11)-C(12) | 119.68(18) |
| C(11)-C(12)-C(8) | 110.72(17) |
| C(11)-C(12)-C(13) | 109.94(17) |
| C(8)-C(12)-C(13) | 108.08(16) |
| C(11)-C(12)-C(14) | 108.34(16) |
| C(8)-C(12)-C(14) | 112.30(16) |
| C(13)-C(12)-C(14) | 107.40(17) |
| C(5)-C(13)-C(12) | 110.68(17) |
| C(5)-C(13)-H(13A) | 109.5 |
| C(12)-C(13)-H(13A) | 109.5 |
| C(5)-C(13)-H(13B) | 109.5 |
| C(12)-C(13)-H(13B) | 109.5 |
| H(13A)-C(13)-H(13B) | 108.1 |
| O(5)-C(14)-C(15) | 110.53(17) |
| O(5)-C(14)-C(12) | 109.68(17) |
| C(15)-C(14)-C(12) | 113.04(17) |
| O(5)-C(14)-H(14) | 107.8 |
| C(15)-C(14)-H(14) | 107.8 |
| C(12)-C(14)-H(14) | 107.8 |
| C(16)-C(15)-C(14) | 125.09(19) |
| C(16)-C(15)-H(15) | 117.5 |
| C(14)-C(15)-H(15) | 117.5 |
| C(15)-C(16)-C(23) | 121.44(19) |

| | |
|---|---|
| C(15)-C(16)-C(17) | 121.46(19) |
| C(23)-C(16)-C(17) | 117.09(19) |
| C(18)-C(17)-C(22) | 118.9(2) |
| C(18)-C(17)-C(16) | 120.0(2) |
| C(22)-C(17)-C(16) | 121.0(2) |
| C(17)-C(18)-C(19) | 120.8(2) |
| C(17)-C(18)-H(18) | 119.6 |
| C(19)-C(18)-H(18) | 119.6 |
| C(20)-C(19)-C(18) | 119.6(3) |
| C(20)-C(19)-H(19) | 120.2 |
| C(18)-C(19)-H(19) | 120.2 |
| C(21)-C(20)-C(19) | 120.3(2) |
| C(21)-C(20)-H(20) | 119.8 |
| C(19)-C(20)-H(20) | 119.8 |
| C(20)-C(21)-C(22) | 120.6(3) |
| C(20)-C(21)-H(21) | 119.7 |
| C(22)-C(21)-H(21) | 119.7 |
| C(17)-C(22)-C(21) | 119.8(3) |
| C(17)-C(22)-H(22) | 120.1 |
| C(21)-C(22)-H(22) | 120.1 |
| C(24)-C(23)-C(28) | 118.7(2) |
| C(24)-C(23)-C(16) | 120.4(2) |
| C(28)-C(23)-C(16) | 120.9(2) |
| C(25)-C(24)-C(23) | 120.6(2) |
| C(25)-C(24)-H(24) | 119.7 |
| C(23)-C(24)-H(24) | 119.7 |
| C(26)-C(25)-C(24) | 120.2(2) |
| C(26)-C(25)-H(25) | 119.9 |
| C(24)-C(25)-H(25) | 119.9 |
| C(25)-C(26)-C(27) | 119.8(2) |
| C(25)-C(26)-H(26) | 120.1 |
| C(27)-C(26)-H(26) | 120.1 |
| C(26)-C(27)-C(28) | 120.5(2) |
| C(26)-C(27)-H(27) | 119.8 |
| C(28)-C(27)-H(27) | 119.8 |
| C(27)-C(28)-C(23) | 120.3(2) |
| C(27)-C(28)-H(28) | 119.9 |
| C(23)-C(28)-H(28) | 119.9 |
| Cl(1)-C(29)-Cl(2) | 112.09(16) |
| Cl(1)-C(29)-H(29A) | 109.2 |
| Cl(2)-C(29)-H(29A) | 109.2 |
| Cl(1)-C(29)-H(29B) | 109.2 |
| Cl(2)-C(29)-H(29B) | 109.2 |
| H(29A)-C(29)-H(29B) | 107.9 |

Table C.4q Anisotropic displacement parameters (A^2 x 10^3) for yddiph. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Cl(1) | 62(1) | 100(1) | 56(1) | 14(1) | 0(1) | 15(1) |
| Cl(2) | 63(1) | 47(1) | 83(1) | -7(1) | -37(1) | -1(1) |
| O(1) | 30(1) | 44(1) | 33(1) | 11(1) | 4(1) | 5(1) |
| O(2) | 31(1) | 37(1) | 45(1) | 7(1) | 9(1) | 7(1) |
| O(3) | 23(1) | 40(1) | 35(1) | 1(1) | -2(1) | 2(1) |
| O(4) | 20(1) | 34(1) | 46(1) | 6(1) | 6(1) | 4(1) |
| O(5) | 30(1) | 26(1) | 37(1) | -7(1) | 8(1) | -3(1) |
| C(1) | 38(1) | 60(2) | 40(2) | 19(1) | 1(1) | 10(1) |
| C(2) | 25(1) | 30(1) | 37(1) | 7(1) | 5(1) | -2(1) |
| C(3) | 21(1) | 29(1) | 34(1) | 4(1) | 3(1) | -2(1) |
| C(4) | 30(1) | 31(1) | 41(1) | -1(1) | 1(1) | -8(1) |
| C(5) | 31(1) | 31(1) | 34(1) | -4(1) | -4(1) | -4(1) |
| C(6) | 26(1) | 38(1) | 40(1) | -1(1) | -7(1) | -2(1) |
| C(7) | 18(1) | 32(1) | 36(1) | 2(1) | -1(1) | 2(1) |
| C(8) | 19(1) | 25(1) | 30(1) | 0(1) | 2(1) | 0(1) |
| C(9) | 26(1) | 32(1) | 30(1) | -2(1) | 4(1) | 1(1) |
| C(10) | 30(1) | 41(1) | 32(1) | -7(1) | -2(1) | 2(1) |
| C(11) | 22(1) | 26(1) | 34(1) | 2(1) | 2(1) | -1(1) |
| C(12) | 19(1) | 23(1) | 29(1) | 0(1) | 1(1) | 0(1) |
| C(13) | 27(1) | 25(1) | 30(1) | -2(1) | 3(1) | 0(1) |
| C(14) | 21(1) | 24(1) | 30(1) | 0(1) | 2(1) | 0(1) |
| C(15) | 22(1) | 24(1) | 33(1) | -2(1) | 2(1) | -1(1) |
| C(16) | 25(1) | 21(1) | 33(1) | 0(1) | 5(1) | 0(1) |
| C(17) | 26(1) | 32(1) | 31(1) | 8(1) | 4(1) | 2(1) |
| C(18) | 29(1) | 41(1) | 32(1) | 5(1) | 0(1) | -1(1) |
| C(19) | 37(1) | 65(2) | 34(1) | 14(1) | -6(1) | -10(1) |
| C(20) | 29(1) | 82(2) | 43(2) | 27(2) | -5(1) | 2(1) |
| C(21) | 38(1) | 66(2) | 56(2) | 24(2) | 3(1) | 20(1) |
| C(22) | 39(1) | 40(1) | 45(2) | 10(1) | 6(1) | 10(1) |
| C(23) | 26(1) | 24(1) | 33(1) | -5(1) | 4(1) | -3(1) |
| C(24) | 35(1) | 29(1) | 41(1) | 1(1) | 9(1) | -2(1) |
| C(25) | 44(1) | 37(1) | 44(2) | 1(1) | 16(1) | -7(1) |
| C(26) | 32(1) | 44(1) | 50(2) | -12(1) | 16(1) | -8(1) |
| C(27) | 27(1) | 42(1) | 43(1) | -12(1) | 6(1) | -1(1) |
| C(28) | 27(1) | 30(1) | 36(1) | -6(1) | 3(1) | -2(1) |
| C(29) | 35(1) | 63(2) | 64(2) | -6(2) | -6(1) | -14(1) |

Table C.5q Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for yddiph.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(5) | 8039(18) | 1130(30) | 5714(18) | 67(11) |
| H(1A) | 7727 | 5797 | 4074 | 69 |
| H(1B) | 8218 | 6016 | 3517 | 69 |
| H(1C) | 8105 | 6990 | 4037 | 69 |
| H(3) | 9461 | 5195 | 5057 | 33 |
| H(4A) | 9693 | 6000 | 5943 | 41 |
| H(4B) | 8989 | 6504 | 5985 | 41 |
| H(5A) | 9166 | 5403 | 6895 | 38 |
| H(6A) | 9437 | 3383 | 6783 | 41 |
| H(6B) | 9988 | 4212 | 6530 | 41 |
| H(7A) | 9882 | 3555 | 5555 | 34 |
| H(7B) | 9454 | 2547 | 5843 | 34 |
| H(9A) | 9105 | 3631 | 4492 | 35 |
| H(9B) | 9001 | 2441 | 4856 | 35 |
| H(10A) | 8162 | 3399 | 4116 | 42 |
| H(10B) | 8013 | 2371 | 4592 | 42 |
| H(13A) | 8134 | 5272 | 6382 | 33 |
| H(13B) | 8283 | 4193 | 6828 | 33 |
| H(14) | 8607 | 2357 | 6429 | 30 |
| H(15) | 7257 | 2393 | 6286 | 32 |
| H(18) | 8061 | 3556 | 8011 | 41 |
| H(19) | 9028 | 3537 | 8544 | 54 |
| H(20) | 9734 | 2023 | 8383 | 61 |
| H(21) | 9473 | 518 | 7716 | 64 |
| H(22) | 8514 | 538 | 7165 | 50 |
| H(24) | 7283 | 890 | 8112 | 42 |
| H(25) | 6310 | 701 | 8621 | 50 |
| H(26) | 5442 | 1779 | 8290 | 50 |
| H(27) | 5543 | 3040 | 7444 | 45 |
| H(28) | 6509 | 3230 | 6924 | 37 |
| H(29A) | 6253 | 4213 | 5571 | 65 |
| H(29B) | 5833 | 5237 | 5288 | 65 |

Table C.6q Torsion angles [deg] for yddiph.

| | |
|---|---|
| C(1)-O(1)-C(2)-O(2) | -5.9(3) |
| C(1)-O(1)-C(2)-C(3) | 173.7(2) |

| | |
|---|---|
| O(2)-C(2)-C(3)-C(4) | -30.0(3) |
| O(1)-C(2)-C(3)-C(4) | 150.40(18) |
| O(2)-C(2)-C(3)-C(8) | 96.8(3) |
| O(1)-C(2)-C(3)-C(8) | -82.9(2) |
| C(2)-C(3)-C(4)-C(5) | 119.7(2) |
| C(8)-C(3)-C(4)-C(5) | -9.0(2) |
| C(3)-C(4)-C(5)-C(6) | 66.0(2) |
| C(3)-C(4)-C(5)-C(13) | -54.4(2) |
| C(4)-C(5)-C(6)-C(7) | -53.8(2) |
| C(13)-C(5)-C(6)-C(7) | 64.7(2) |
| C(5)-C(6)-C(7)-C(8) | -12.2(2) |
| C(6)-C(7)-C(8)-C(9) | -175.72(18) |
| C(6)-C(7)-C(8)-C(12) | -51.5(2) |
| C(6)-C(7)-C(8)-C(3) | 66.1(2) |
| C(2)-C(3)-C(8)-C(9) | 60.6(2) |
| C(4)-C(3)-C(8)-C(9) | -172.16(17) |
| C(2)-C(3)-C(8)-C(7) | 179.02(18) |
| C(4)-C(3)-C(8)-C(7) | -53.7(2) |
| C(2)-C(3)-C(8)-C(12) | -64.5(2) |
| C(4)-C(3)-C(8)-C(12) | 62.8(2) |
| C(7)-C(8)-C(9)-C(10) | 152.12(19) |
| C(12)-C(8)-C(9)-C(10) | 30.5(3) |
| C(3)-C(8)-C(9)-C(10) | -92.9(2) |
| C(11)-O(3)-C(10)-C(9) | -38.4(3) |
| C(8)-C(9)-C(10)-O(3) | 11.5(3) |
| C(10)-O(3)-C(11)-O(4) | -165.1(2) |
| C(10)-O(3)-C(11)-C(12) | 17.1(3) |
| O(4)-C(11)-C(12)-C(8) | -150.1(2) |
| O(3)-C(11)-C(12)-C(8) | 27.6(3) |
| O(4)-C(11)-C(12)-C(13) | -30.7(3) |
| O(3)-C(11)-C(12)-C(13) | 146.95(19) |
| O(4)-C(11)-C(12)-C(14) | 86.4(2) |
| O(3)-C(11)-C(12)-C(14) | -96.0(2) |
| C(9)-C(8)-C(12)-C(11) | -50.2(2) |
| C(7)-C(8)-C(12)-C(11) | -172.70(17) |
| C(3)-C(8)-C(12)-C(11) | 73.1(2) |
| C(9)-C(8)-C(12)-C(13) | -170.63(17) |
| C(7)-C(8)-C(12)-C(13) | 66.8(2) |
| C(3)-C(8)-C(12)-C(13) | -47.3(2) |
| C(9)-C(8)-C(12)-C(14) | 71.1(2) |
| C(7)-C(8)-C(12)-C(14) | -51.5(2) |
| C(3)-C(8)-C(12)-C(14) | -165.63(17) |
| C(6)-C(5)-C(13)-C(12) | -48.8(3) |
| C(4)-C(5)-C(13)-C(12) | 70.1(2) |
| C(11)-C(12)-C(13)-C(5) | -136.60(19) |
| C(8)-C(12)-C(13)-C(5) | -15.6(2) |

| | |
|---|---|
| C(14)-C(12)-C(13)-C(5) | 105.73(19) |
| C(11)-C(12)-C(14)-O(5) | 71.6(2) |
| C(8)-C(12)-C(14)-O(5) | -51.0(2) |
| C(13)-C(12)-C(14)-O(5) | -169.72(15) |
| C(11)-C(12)-C(14)-C(15) | -52.3(2) |
| C(8)-C(12)-C(14)-C(15) | -174.87(17) |
| C(13)-C(12)-C(14)-C(15) | 66.4(2) |
| O(5)-C(14)-C(15)-C(16) | 123.8(2) |
| C(12)-C(14)-C(15)-C(16) | -112.8(2) |
| C(14)-C(15)-C(16)-C(23) | 177.83(19) |
| C(14)-C(15)-C(16)-C(17) | -1.0(3) |
| C(15)-C(16)-C(17)-C(18) | 109.8(3) |
| C(23)-C(16)-C(17)-C(18) | -69.2(3) |
| C(15)-C(16)-C(17)-C(22) | -66.4(3) |
| C(23)-C(16)-C(17)-C(22) | 114.7(2) |
| C(22)-C(17)-C(18)-C(19) | 2.8(3) |
| C(16)-C(17)-C(18)-C(19) | -173.4(2) |
| C(17)-C(18)-C(19)-C(20) | -1.2(4) |
| C(18)-C(19)-C(20)-C(21) | -0.9(4) |
| C(19)-C(20)-C(21)-C(22) | 1.5(4) |
| C(18)-C(17)-C(22)-C(21) | -2.2(4) |
| C(16)-C(17)-C(22)-C(21) | 174.0(2) |
| C(20)-C(21)-C(22)-C(17) | 0.1(4) |
| C(15)-C(16)-C(23)-C(24) | 146.1(2) |
| C(17)-C(16)-C(23)-C(24) | -35.0(3) |
| C(15)-C(16)-C(23)-C(28) | -34.2(3) |
| C(17)-C(16)-C(23)-C(28) | 144.8(2) |
| C(28)-C(23)-C(24)-C(25) | 1.1(3) |
| C(16)-C(23)-C(24)-C(25) | -179.1(2) |
| C(23)-C(24)-C(25)-C(26) | -0.8(4) |
| C(24)-C(25)-C(26)-C(27) | 0.1(4) |
| C(25)-C(26)-C(27)-C(28) | 0.1(4) |
| C(26)-C(27)-C(28)-C(23) | 0.2(4) |
| C(24)-C(23)-C(28)-C(27) | -0.9(3) |
| C(16)-C(23)-C(28)-C(27) | 179.3(2) |

Table C.7q Hydrogen bonds for yddiph [A and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(5)-H(5)...O(4)#1 | 0.83(4) | 2.02(4) | 2.813(2) | 160(4) |

Symmetry transformations used to generate equivalent atoms:
#1 -x+3/2,y-1/2,z

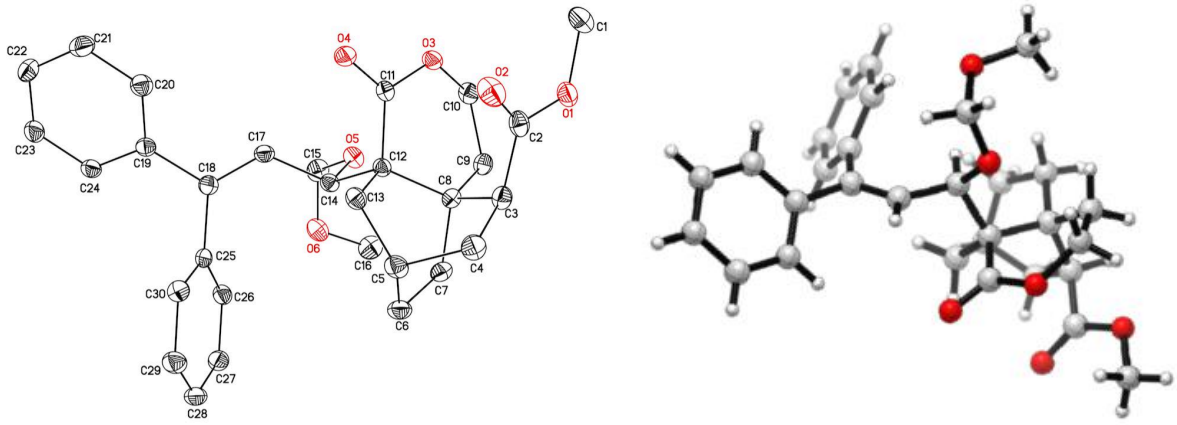



Figure C.18 Structure of yddiphm.

**Structure Determination.**

Colorless plates of **yddiphm** were grown from a dichloromethane/hexanes solution of the compound at 22 deg. C. A crystal of dimensions 0.26 x 0.19 x 0.18 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (ë = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ù. The exposure times were 1 sec. for the low angle images, 4 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 57628 reflections to a maximum 2è value of 138.50° of which 4714 were independent and 4703 were greater than 2ó(I). The final cell constants (Table 1) were based on the xyz centroids 57628 reflections above 10ó(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group Pbca with Z = 8 for the formula $C_{30}H_{34}O_6$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on $F^2$ converged at R1 = 0.0465 and wR2 = 0.1097 [based on I > 2sigma(I)], R1 = 0.0466 and wR2 = 0.1098 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Sheldrick, G.M. SHELXTL, v. 2014/6; Bruker Analytical X-ray, Madison, WI, 2014.
CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.
CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015).

Table C.1r Crystal data and structure refinement for yddiphm.

| | |
|---|---|
| Identification code | yddiphm |
| Empirical formula | C30 H34 O6 |
| Formula weight | 490.57 |
| Temperature | 85(2) K |

| | |
|---|---|
| Wavelength | 1.54184 A |
| Crystal system, space group | Orthorhombic, Pbca |
| Unit cell dimensions | a = 11.63900(10) A alpha = 90 deg. |
| | b = 18.82240(10) A beta = 90 deg. |
| | c = 23.11190(10) A gamma = 90 deg. |
| Volume | 5063.21(3) A^3 |
| Z, Calculated density | 8, 1.287 Mg/m^3 |
| Absorption coefficient | 0.718 mm^-1 |
| F(000) | 2096 |
| Crystal size | 0.260 x 0.190 x 0.180 mm |
| Theta range for data collection | 3.825 to 69.251 deg. |
| Limiting indices | -13<=h<=14, -20<=k<=22, -27<=l<=27 |
| Reflections collected / unique | 74508 / 4714 [R(int) = 0.0596] |
| Completeness to theta = 67.684 | 100.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00000 and 0.89528 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 4714 / 0 / 328 |
| Goodness-of-fit on F^2 | 1.139 |
| Final R indices [I>2sigma(I)] | R1 = 0.0465, wR2 = 0.1097 |
| R indices (all data) | R1 = 0.0466, wR2 = 0.1098 |
| Extinction coefficient | 0.0071(3) |
| Largest diff. peak and hole | 0.398 and -0.438 e.A^-3 |

Table C.2r Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for yddiphm. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 6115(1) | 4805(1) | 7302(1) | 21(1) |
| O(2) | 4722(1) | 5072(1) | 6667(1) | 27(1) |
| O(3) | 5633(1) | 6352(1) | 7484(1) | 18(1) |
| O(4) | 4326(1) | 6767(1) | 6891(1) | 21(1) |
| O(5) | 7190(1) | 7546(1) | 7001(1) | 19(1) |
| O(6) | 8656(1) | 8306(1) | 6677(1) | 24(1) |
| C(1) | 5235(1) | 4650(1) | 7724(1) | 28(1) |
| C(2) | 5728(1) | 5046(1) | 6791(1) | 19(1) |
| C(3) | 6713(1) | 5286(1) | 6408(1) | 18(1) |
| C(4) | 6392(1) | 5238(1) | 5757(1) | 22(1) |
| C(5) | 6379(1) | 5986(1) | 5502(1) | 20(1) |
| C(6) | 7609(1) | 6271(1) | 5494(1) | 21(1) |
| C(7) | 8123(1) | 6196(1) | 6108(1) | 20(1) |
| C(8) | 7171(1) | 6053(1) | 6561(1) | 16(1) |
| C(9) | 7674(1) | 6067(1) | 7175(1) | 18(1) |

| | | | | |
|---|---|---|---|---|
| C(10) | 6835(1) | 6274(1) | 7656(1) | 19(1) |
| C(11) | 5311(1) | 6586(1) | 6959(1) | 16(1) |
| C(12) | 6197(1) | 6614(1) | 6473(1) | 14(1) |
| C(13) | 5607(1) | 6452(1) | 5882(1) | 17(1) |
| C(14) | 6636(1) | 7402(1) | 6456(1) | 15(1) |
| C(15) | 7707(1) | 8224(1) | 7041(1) | 23(1) |
| C(16) | 9647(1) | 7933(1) | 6873(1) | 29(1) |
| C(17) | 5679(1) | 7929(1) | 6366(1) | 17(1) |
| C(18) | 5471(1) | 8320(1) | 5893(1) | 16(1) |
| C(19) | 4473(1) | 8815(1) | 5884(1) | 16(1) |
| C(20) | 3410(1) | 8621(1) | 6118(1) | 20(1) |
| C(21) | 2518(1) | 9110(1) | 6148(1) | 24(1) |
| C(22) | 2671(1) | 9800(1) | 5945(1) | 24(1) |
| C(23) | 3715(1) | 9992(1) | 5702(1) | 22(1) |
| C(24) | 4606(1) | 9504(1) | 5668(1) | 18(1) |
| C(25) | 6202(1) | 8295(1) | 5362(1) | 16(1) |
| C(26) | 7368(1) | 8464(1) | 5383(1) | 18(1) |
| C(27) | 8037(1) | 8432(1) | 4886(1) | 21(1) |
| C(28) | 7559(1) | 8229(1) | 4362(1) | 22(1) |
| C(29) | 6396(1) | 8064(1) | 4337(1) | 23(1) |
| C(30) | 5719(1) | 8099(1) | 4832(1) | 20(1) |

Table C.3r Bond lengths [A] and angles [deg] for yddiphm.

| | |
|---|---|
| O(1)-C(2) | 1.3444(15) |
| O(1)-C(1) | 1.4431(16) |
| O(2)-C(2) | 1.2063(17) |
| O(3)-C(11) | 1.3438(15) |
| O(3)-C(10) | 1.4622(15) |
| O(4)-C(11) | 1.2068(15) |
| O(5)-C(15) | 1.4152(15) |
| O(5)-C(14) | 1.4410(14) |
| O(6)-C(15) | 1.3972(16) |
| O(6)-C(16) | 1.4232(18) |
| C(1)-H(1A) | 0.9800 |
| C(1)-H(1B) | 0.9800 |
| C(1)-H(1C) | 0.9800 |
| C(2)-C(3) | 1.5169(18) |
| C(3)-C(4) | 1.5515(17) |
| C(3)-C(8) | 1.5796(16) |
| C(3)-H(3) | 1.0000 |
| C(4)-C(5) | 1.5268(18) |
| C(4)-H(4A) | 0.9900 |
| C(4)-H(4B) | 0.9900 |

| | |
|---|---|
| C(5)-C(6) | 1.5289(18) |
| C(5)-C(13) | 1.5325(17) |
| C(5)-H(5) | 1.0000 |
| C(6)-C(7) | 1.5471(18) |
| C(6)-H(6A) | 0.9900 |
| C(6)-H(6B) | 0.9900 |
| C(7)-C(8) | 1.5467(17) |
| C(7)-H(7A) | 0.9900 |
| C(7)-H(7B) | 0.9900 |
| C(8)-C(9) | 1.5354(16) |
| C(8)-C(12) | 1.5625(16) |
| C(9)-C(10) | 1.5307(17) |
| C(9)-H(9A) | 0.9900 |
| C(9)-H(9B) | 0.9900 |
| C(10)-H(10A) | 0.9900 |
| C(10)-H(10B) | 0.9900 |
| C(11)-C(12) | 1.5252(16) |
| C(12)-C(13) | 1.5588(16) |
| C(12)-C(14) | 1.5691(16) |
| C(13)-H(13A) | 0.9900 |
| C(13)-H(13B) | 0.9900 |
| C(14)-C(17) | 1.5057(16) |
| C(14)-H(14) | 1.0000 |
| C(15)-H(15A) | 0.9900 |
| C(15)-H(15B) | 0.9900 |
| C(16)-H(16A) | 0.9800 |
| C(16)-H(16B) | 0.9800 |
| C(16)-H(16C) | 0.9800 |
| C(17)-C(18) | 1.3396(18) |
| C(17)-H(17) | 0.9500 |
| C(18)-C(19) | 1.4897(17) |
| C(18)-C(25) | 1.4936(16) |
| C(19)-C(20) | 1.3980(18) |
| C(19)-C(24) | 1.3984(17) |
| C(20)-C(21) | 1.3891(19) |
| C(20)-H(20) | 0.9500 |
| C(21)-C(22) | 1.3923(19) |
| C(21)-H(21) | 0.9500 |
| C(22)-C(23) | 1.3870(19) |
| C(22)-H(22) | 0.9500 |
| C(23)-C(24) | 1.3874(18) |
| C(23)-H(23) | 0.9500 |
| C(24)-H(24) | 0.9500 |
| C(25)-C(26) | 1.3950(18) |
| C(25)-C(30) | 1.3975(18) |
| C(26)-C(27) | 1.3899(18) |

| | |
|---|---|
| C(26)-H(26) | 0.9500 |
| C(27)-C(28) | 1.3857(19) |
| C(27)-H(27) | 0.9500 |
| C(28)-C(29) | 1.390(2) |
| C(28)-H(28) | 0.9500 |
| C(29)-C(30) | 1.3906(18) |
| C(29)-H(29) | 0.9500 |
| C(30)-H(30) | 0.9500 |
| C(2)-O(1)-C(1) | 115.08(10) |
| C(11)-O(3)-C(10) | 123.06(9) |
| C(15)-O(5)-C(14) | 114.63(9) |
| C(15)-O(6)-C(16) | 113.27(10) |
| O(1)-C(1)-H(1A) | 109.5 |
| O(1)-C(1)-H(1B) | 109.5 |
| H(1A)-C(1)-H(1B) | 109.5 |
| O(1)-C(1)-H(1C) | 109.5 |
| H(1A)-C(1)-H(1C) | 109.5 |
| H(1B)-C(1)-H(1C) | 109.5 |
| O(2)-C(2)-O(1) | 123.20(12) |
| O(2)-C(2)-C(3) | 125.63(12) |
| O(1)-C(2)-C(3) | 111.16(11) |
| C(2)-C(3)-C(4) | 111.49(10) |
| C(2)-C(3)-C(8) | 113.35(10) |
| C(4)-C(3)-C(8) | 110.57(10) |
| C(2)-C(3)-H(3) | 107.0 |
| C(4)-C(3)-H(3) | 107.0 |
| C(8)-C(3)-H(3) | 107.0 |
| C(5)-C(4)-C(3) | 108.88(10) |
| C(5)-C(4)-H(4A) | 109.9 |
| C(3)-C(4)-H(4A) | 109.9 |
| C(5)-C(4)-H(4B) | 109.9 |
| C(3)-C(4)-H(4B) | 109.9 |
| H(4A)-C(4)-H(4B) | 108.3 |
| C(4)-C(5)-C(6) | 108.55(11) |
| C(4)-C(5)-C(13) | 108.20(10) |
| C(6)-C(5)-C(13) | 110.73(10) |
| C(4)-C(5)-H(5) | 109.8 |
| C(6)-C(5)-H(5) | 109.8 |
| C(13)-C(5)-H(5) | 109.8 |
| C(5)-C(6)-C(7) | 108.68(10) |
| C(5)-C(6)-H(6A) | 110.0 |
| C(7)-C(6)-H(6A) | 110.0 |
| C(5)-C(6)-H(6B) | 110.0 |
| C(7)-C(6)-H(6B) | 110.0 |
| H(6A)-C(6)-H(6B) | 108.3 |
| C(8)-C(7)-C(6) | 111.00(10) |

| | |
|---|---|
| C(8)-C(7)-H(7A) | 109.4 |
| C(6)-C(7)-H(7A) | 109.4 |
| C(8)-C(7)-H(7B) | 109.4 |
| C(6)-C(7)-H(7B) | 109.4 |
| H(7A)-C(7)-H(7B) | 108.0 |
| C(9)-C(8)-C(7) | 110.37(10) |
| C(9)-C(8)-C(12) | 112.63(9) |
| C(7)-C(8)-C(12) | 108.34(9) |
| C(9)-C(8)-C(3) | 110.58(10) |
| C(7)-C(8)-C(3) | 104.46(10) |
| C(12)-C(8)-C(3) | 110.12(9) |
| C(10)-C(9)-C(8) | 115.68(10) |
| C(10)-C(9)-H(9A) | 108.4 |
| C(8)-C(9)-H(9A) | 108.4 |
| C(10)-C(9)-H(9B) | 108.4 |
| C(8)-C(9)-H(9B) | 108.4 |
| H(9A)-C(9)-H(9B) | 107.4 |
| O(3)-C(10)-C(9) | 115.93(10) |
| O(3)-C(10)-H(10A) | 108.3 |
| C(9)-C(10)-H(10A) | 108.3 |
| O(3)-C(10)-H(10B) | 108.3 |
| C(9)-C(10)-H(10B) | 108.3 |
| H(10A)-C(10)-H(10B) | 107.4 |
| O(4)-C(11)-O(3) | 118.33(11) |
| O(4)-C(11)-C(12) | 122.48(11) |
| O(3)-C(11)-C(12) | 119.19(10) |
| C(11)-C(12)-C(13) | 109.94(9) |
| C(11)-C(12)-C(8) | 111.80(9) |
| C(13)-C(12)-C(8) | 107.52(9) |
| C(11)-C(12)-C(14) | 105.76(9) |
| C(13)-C(12)-C(14) | 107.80(9) |
| C(8)-C(12)-C(14) | 113.94(9) |
| C(5)-C(13)-C(12) | 110.89(10) |
| C(5)-C(13)-H(13A) | 109.5 |
| C(12)-C(13)-H(13A) | 109.5 |
| C(5)-C(13)-H(13B) | 109.5 |
| C(12)-C(13)-H(13B) | 109.5 |
| H(13A)-C(13)-H(13B) | 108.0 |
| O(5)-C(14)-C(17) | 109.17(9) |
| O(5)-C(14)-C(12) | 107.50(9) |
| C(17)-C(14)-C(12) | 112.65(10) |
| O(5)-C(14)-H(14) | 109.2 |
| C(17)-C(14)-H(14) | 109.2 |
| C(12)-C(14)-H(14) | 109.2 |
| O(6)-C(15)-O(5) | 113.31(10) |
| O(6)-C(15)-H(15A) | 108.9 |

| | |
|---|---|
| O(5)-C(15)-H(15A) | 108.9 |
| O(6)-C(15)-H(15B) | 108.9 |
| O(5)-C(15)-H(15B) | 108.9 |
| H(15A)-C(15)-H(15B) | 107.7 |
| O(6)-C(16)-H(16A) | 109.5 |
| O(6)-C(16)-H(16B) | 109.5 |
| H(16A)-C(16)-H(16B) | 109.5 |
| O(6)-C(16)-H(16C) | 109.5 |
| H(16A)-C(16)-H(16C) | 109.5 |
| H(16B)-C(16)-H(16C) | 109.5 |
| C(18)-C(17)-C(14) | 127.48(11) |
| C(18)-C(17)-H(17) | 116.3 |
| C(14)-C(17)-H(17) | 116.3 |
| C(17)-C(18)-C(19) | 119.71(11) |
| C(17)-C(18)-C(25) | 123.30(11) |
| C(19)-C(18)-C(25) | 116.99(10) |
| C(20)-C(19)-C(24) | 118.54(11) |
| C(20)-C(19)-C(18) | 121.47(11) |
| C(24)-C(19)-C(18) | 119.90(11) |
| C(21)-C(20)-C(19) | 120.54(12) |
| C(21)-C(20)-H(20) | 119.7 |
| C(19)-C(20)-H(20) | 119.7 |
| C(20)-C(21)-C(22) | 120.33(12) |
| C(20)-C(21)-H(21) | 119.8 |
| C(22)-C(21)-H(21) | 119.8 |
| C(23)-C(22)-C(21) | 119.49(12) |
| C(23)-C(22)-H(22) | 120.3 |
| C(21)-C(22)-H(22) | 120.3 |
| C(22)-C(23)-C(24) | 120.30(12) |
| C(22)-C(23)-H(23) | 119.9 |
| C(24)-C(23)-H(23) | 119.9 |
| C(23)-C(24)-C(19) | 120.77(12) |
| C(23)-C(24)-H(24) | 119.6 |
| C(19)-C(24)-H(24) | 119.6 |
| C(26)-C(25)-C(30) | 118.88(11) |
| C(26)-C(25)-C(18) | 121.17(11) |
| C(30)-C(25)-C(18) | 119.95(11) |
| C(27)-C(26)-C(25) | 120.37(12) |
| C(27)-C(26)-H(26) | 119.8 |
| C(25)-C(26)-H(26) | 119.8 |
| C(28)-C(27)-C(26) | 120.68(12) |
| C(28)-C(27)-H(27) | 119.7 |
| C(26)-C(27)-H(27) | 119.7 |
| C(27)-C(28)-C(29) | 119.21(12) |
| C(27)-C(28)-H(28) | 120.4 |
| C(29)-C(28)-H(28) | 120.4 |

| | |
|---|---|
| C(28)-C(29)-C(30) | 120.53(12) |
| C(28)-C(29)-H(29) | 119.7 |
| C(30)-C(29)-H(29) | 119.7 |
| C(29)-C(30)-C(25) | 120.32(12) |
| C(29)-C(30)-H(30) | 119.8 |
| C(25)-C(30)-H(30) | 119.8 |

Table C.4r Anisotropic displacement parameters (A^2 x 10^3) for yddiphm. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| O(1) | 25(1) | 18(1) | 20(1) | 4(1) | -1(1) | 1(1) |
| O(2) | 22(1) | 29(1) | 28(1) | 6(1) | -5(1) | -7(1) |
| O(3) | 17(1) | 22(1) | 14(1) | 3(1) | 0(1) | 1(1) |
| O(4) | 15(1) | 25(1) | 22(1) | 5(1) | 2(1) | 2(1) |
| O(5) | 24(1) | 17(1) | 16(1) | -1(1) | -2(1) | -4(1) |
| O(6) | 26(1) | 23(1) | 24(1) | 2(1) | -2(1) | -6(1) |
| C(1) | 31(1) | 27(1) | 26(1) | 9(1) | 4(1) | -1(1) |
| C(2) | 24(1) | 13(1) | 20(1) | 0(1) | -3(1) | -2(1) |
| C(3) | 20(1) | 16(1) | 19(1) | -1(1) | -2(1) | 1(1) |
| C(4) | 28(1) | 19(1) | 18(1) | -4(1) | -2(1) | 0(1) |
| C(5) | 25(1) | 21(1) | 14(1) | -2(1) | -1(1) | -1(1) |
| C(6) | 24(1) | 23(1) | 17(1) | -2(1) | 5(1) | 1(1) |
| C(7) | 16(1) | 21(1) | 21(1) | -2(1) | 3(1) | 2(1) |
| C(8) | 15(1) | 16(1) | 16(1) | -1(1) | 0(1) | 1(1) |
| C(9) | 16(1) | 19(1) | 19(1) | 0(1) | -4(1) | 1(1) |
| C(10) | 19(1) | 22(1) | 15(1) | 2(1) | -4(1) | 0(1) |
| C(11) | 17(1) | 14(1) | 16(1) | 1(1) | -1(1) | -1(1) |
| C(12) | 14(1) | 15(1) | 14(1) | 1(1) | 0(1) | 0(1) |
| C(13) | 17(1) | 18(1) | 15(1) | 2(1) | -3(1) | -1(1) |
| C(14) | 17(1) | 15(1) | 14(1) | 0(1) | 0(1) | -1(1) |
| C(15) | 25(1) | 18(1) | 25(1) | -5(1) | -1(1) | -4(1) |
| C(16) | 24(1) | 29(1) | 34(1) | -3(1) | -1(1) | -4(1) |
| C(17) | 19(1) | 16(1) | 16(1) | -1(1) | 4(1) | 0(1) |
| C(18) | 18(1) | 13(1) | 17(1) | -1(1) | 1(1) | -1(1) |
| C(19) | 20(1) | 17(1) | 12(1) | -2(1) | 1(1) | 1(1) |
| C(20) | 21(1) | 18(1) | 21(1) | 0(1) | 2(1) | -1(1) |
| C(21) | 19(1) | 27(1) | 26(1) | 0(1) | 5(1) | 1(1) |
| C(22) | 23(1) | 23(1) | 24(1) | 0(1) | 2(1) | 8(1) |
| C(23) | 28(1) | 17(1) | 19(1) | 2(1) | 2(1) | 4(1) |
| C(24) | 21(1) | 19(1) | 15(1) | 0(1) | 3(1) | 1(1) |
| C(25) | 20(1) | 11(1) | 17(1) | 1(1) | 3(1) | 3(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(26) | 21(1) | 16(1) | 18(1) | 2(1) | 1(1) | 0(1) |
| C(27) | 20(1) | 19(1) | 24(1) | 2(1) | 4(1) | 0(1) |
| C(28) | 27(1) | 18(1) | 19(1) | 0(1) | 9(1) | 2(1) |
| C(29) | 29(1) | 22(1) | 17(1) | -3(1) | 1(1) | 1(1) |
| C(30) | 19(1) | 20(1) | 20(1) | 0(1) | 2(1) | 1(1) |

Table C.5r Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for yddiphm.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 4858 | 5092 | 7841 | 42 |
| H(1B) | 5584 | 4423 | 8063 | 42 |
| H(1C) | 4666 | 4328 | 7553 | 42 |
| H(3) | 7362 | 4947 | 6474 | 22 |
| H(4A) | 6960 | 4941 | 5550 | 26 |
| H(4B) | 5626 | 5016 | 5713 | 26 |
| H(5) | 6068 | 5971 | 5098 | 24 |
| H(6A) | 7610 | 6776 | 5375 | 25 |
| H(6B) | 8077 | 5998 | 5214 | 25 |
| H(7A) | 8682 | 5800 | 6113 | 23 |
| H(7B) | 8537 | 6638 | 6211 | 23 |
| H(9A) | 7986 | 5590 | 7263 | 21 |
| H(9B) | 8325 | 6405 | 7180 | 21 |
| H(10A) | 6879 | 5910 | 7964 | 23 |
| H(10B) | 7095 | 6730 | 7826 | 23 |
| H(13A) | 4868 | 6206 | 5951 | 20 |
| H(13B) | 5443 | 6904 | 5679 | 20 |
| H(14) | 7210 | 7453 | 6136 | 18 |
| H(15A) | 7128 | 8590 | 6942 | 28 |
| H(15B) | 7951 | 8306 | 7445 | 28 |
| H(16A) | 9822 | 8076 | 7271 | 43 |
| H(16B) | 10301 | 8047 | 6623 | 43 |
| H(16C) | 9499 | 7421 | 6861 | 43 |
| H(17) | 5163 | 7990 | 6680 | 20 |
| H(20) | 3297 | 8151 | 6257 | 24 |
| H(21) | 1800 | 8973 | 6308 | 29 |
| H(22) | 2065 | 10136 | 5973 | 28 |
| H(23) | 3821 | 10461 | 5558 | 26 |
| H(24) | 5314 | 9640 | 5497 | 22 |
| H(26) | 7707 | 8603 | 5740 | 22 |
| H(27) | 8830 | 8549 | 4905 | 25 |
| H(28) | 8021 | 8204 | 4024 | 26 |

| | | | | |
|---|---|---|---|---|
| H(29) | 6061 | 7926 | 3980 | 27 |
| H(30) | 4923 | 7990 | 4810 | 24 |

Table C.6r Torsion angles [deg] for yddiphm.

| | |
|---|---|
| C(1)-O(1)-C(2)-O(2) | -6.59(17) |
| C(1)-O(1)-C(2)-C(3) | 172.43(10) |
| O(2)-C(2)-C(3)-C(4) | -26.86(17) |
| O(1)-C(2)-C(3)-C(4) | 154.15(10) |
| O(2)-C(2)-C(3)-C(8) | 98.68(15) |
| O(1)-C(2)-C(3)-C(8) | -80.31(12) |
| C(2)-C(3)-C(4)-C(5) | 115.13(12) |
| C(8)-C(3)-C(4)-C(5) | -11.93(14) |
| C(3)-C(4)-C(5)-C(6) | 67.86(13) |
| C(3)-C(4)-C(5)-C(13) | -52.37(13) |
| C(4)-C(5)-C(6)-C(7) | -52.68(13) |
| C(13)-C(5)-C(6)-C(7) | 65.97(13) |
| C(5)-C(6)-C(7)-C(8) | -14.99(14) |
| C(6)-C(7)-C(8)-C(9) | -173.38(10) |
| C(6)-C(7)-C(8)-C(12) | -49.63(13) |
| C(6)-C(7)-C(8)-C(3) | 67.73(12) |
| C(2)-C(3)-C(8)-C(9) | 63.34(13) |
| C(4)-C(3)-C(8)-C(9) | -170.63(10) |
| C(2)-C(3)-C(8)-C(7) | -177.92(10) |
| C(4)-C(3)-C(8)-C(7) | -51.89(12) |
| C(2)-C(3)-C(8)-C(12) | -61.78(13) |
| C(4)-C(3)-C(8)-C(12) | 64.25(13) |
| C(7)-C(8)-C(9)-C(10) | 153.01(10) |
| C(12)-C(8)-C(9)-C(10) | 31.78(14) |
| C(3)-C(8)-C(9)-C(10) | -91.91(12) |
| C(11)-O(3)-C(10)-C(9) | -32.81(16) |
| C(8)-C(9)-C(10)-O(3) | 6.90(15) |
| C(10)-O(3)-C(11)-O(4) | -165.43(11) |
| C(10)-O(3)-C(11)-C(12) | 14.49(16) |
| O(4)-C(11)-C(12)-C(13) | -33.72(15) |
| O(3)-C(11)-C(12)-C(13) | 146.36(10) |
| O(4)-C(11)-C(12)-C(8) | -153.06(11) |
| O(3)-C(11)-C(12)-C(8) | 27.02(14) |
| O(4)-C(11)-C(12)-C(14) | 82.40(14) |
| O(3)-C(11)-C(12)-C(14) | -97.52(12) |
| C(9)-C(8)-C(12)-C(11) | -48.74(13) |
| C(7)-C(8)-C(12)-C(11) | -171.12(10) |
| C(3)-C(8)-C(12)-C(11) | 75.20(12) |

| | |
|---|---|
| C(9)-C(8)-C(12)-C(13) | -169.49(10) |
| C(7)-C(8)-C(12)-C(13) | 68.12(12) |
| C(3)-C(8)-C(12)-C(13) | -45.55(12) |
| C(9)-C(8)-C(12)-C(14) | 71.11(12) |
| C(7)-C(8)-C(12)-C(14) | -51.28(13) |
| C(3)-C(8)-C(12)-C(14) | -164.95(9) |
| C(4)-C(5)-C(13)-C(12) | 71.98(12) |
| C(6)-C(5)-C(13)-C(12) | -46.88(13) |
| C(11)-C(12)-C(13)-C(5) | -140.38(10) |
| C(8)-C(12)-C(13)-C(5) | -18.46(13) |
| C(14)-C(12)-C(13)-C(5) | 104.79(11) |
| C(15)-O(5)-C(14)-C(17) | -61.61(13) |
| C(15)-O(5)-C(14)-C(12) | 175.90(10) |
| C(11)-C(12)-C(14)-O(5) | 63.02(11) |
| C(13)-C(12)-C(14)-O(5) | -179.41(9) |
| C(8)-C(12)-C(14)-O(5) | -60.17(12) |
| C(11)-C(12)-C(14)-C(17) | -57.30(12) |
| C(13)-C(12)-C(14)-C(17) | 60.27(12) |
| C(8)-C(12)-C(14)-C(17) | 179.51(10) |
| C(16)-O(6)-C(15)-O(5) | -73.75(14) |
| C(14)-O(5)-C(15)-O(6) | -67.75(14) |
| O(5)-C(14)-C(17)-C(18) | 130.86(13) |
| C(12)-C(14)-C(17)-C(18) | -109.79(14) |
| C(14)-C(17)-C(18)-C(19) | 179.85(11) |
| C(14)-C(17)-C(18)-C(25) | -0.6(2) |
| C(17)-C(18)-C(19)-C(20) | -41.21(17) |
| C(25)-C(18)-C(19)-C(20) | 139.19(12) |
| C(17)-C(18)-C(19)-C(24) | 135.24(12) |
| C(25)-C(18)-C(19)-C(24) | -44.36(16) |
| C(24)-C(19)-C(20)-C(21) | -1.79(18) |
| C(18)-C(19)-C(20)-C(21) | 174.70(12) |
| C(19)-C(20)-C(21)-C(22) | 0.1(2) |
| C(20)-C(21)-C(22)-C(23) | 1.2(2) |
| C(21)-C(22)-C(23)-C(24) | -0.9(2) |
| C(22)-C(23)-C(24)-C(19) | -0.82(19) |
| C(20)-C(19)-C(24)-C(23) | 2.13(18) |
| C(18)-C(19)-C(24)-C(23) | -174.42(11) |
| C(17)-C(18)-C(25)-C(26) | -59.58(17) |
| C(19)-C(18)-C(25)-C(26) | 120.01(13) |
| C(17)-C(18)-C(25)-C(30) | 120.60(14) |
| C(19)-C(18)-C(25)-C(30) | -59.82(15) |
| C(30)-C(25)-C(26)-C(27) | -0.70(17) |
| C(18)-C(25)-C(26)-C(27) | 179.47(11) |
| C(25)-C(26)-C(27)-C(28) | -0.11(19) |
| C(26)-C(27)-C(28)-C(29) | 0.56(19) |
| C(27)-C(28)-C(29)-C(30) | -0.18(19) |

| | |
|---|---|
| C(28)-C(29)-C(30)-C(25) | -0.64(19) |
| C(26)-C(25)-C(30)-C(29) | 1.08(18) |
| C(18)-C(25)-C(30)-C(29) | -179.09(11) |

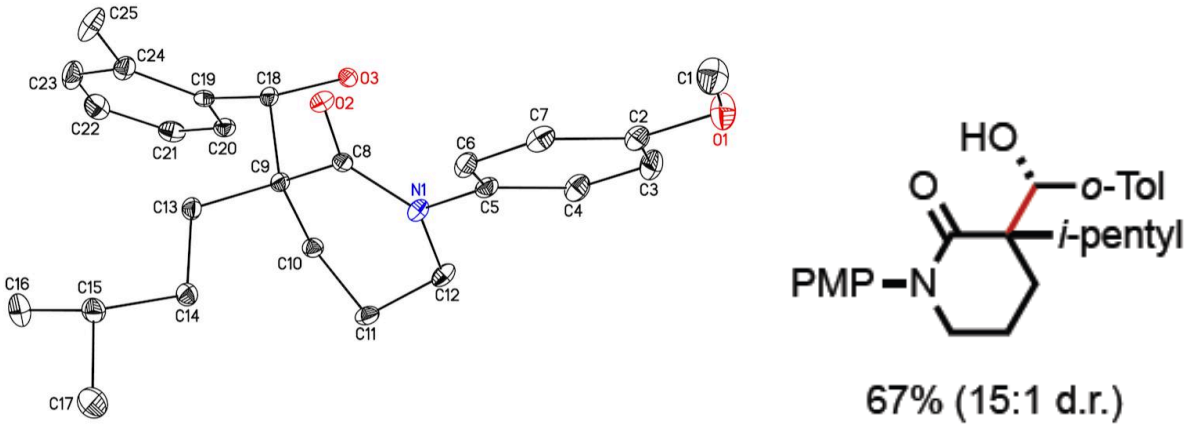



Figure C.19 Structure of ydpmp.

**Structure Determination.**

Colorless plates of **ydpmp** were grown from a dichloromethane/hexanes solution of the compound at 22 deg. C. A crystal of dimensions 0.24 x 0.16 x 0.12 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (ë = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ù. The exposure times were 1 sec. for the low angle images, 3 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 15820 reflections to a maximum 2è value of 138.52° of which 3860 were independent and 3769 were greater than 2ó(I). The final cell constants (Table 1) were based on the xyz centroids 13781 reflections above 10ó(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group P1bar with Z = 2 for the formula $C_{25}H_{33}NO_3$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in a mixture of refined and idealized positions. Full matrix least-squares refinement based on $F^2$ converged at R1 = 0.0496 and wR2 = 0.1224 [based on I > 2sigma(I)], R1 = 0.0502 and wR2 = 0.1230 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.
Sheldrick, G.M. SHELXTL, v. 2014/6; Bruker Analytical X-ray, Madison, WI, 2014.

CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.
CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015).

Table C.1s Crystal data and structure refinement for ydpmp.

| | |
|---|---|
| Identification code | ydpmp |
| Empirical formula | C25 H33 N O3 |
| Formula weight | 395.52 |
| Temperature | 85(2) K |
| Wavelength | 1.54184 A |
| Crystal system, space group | Triclinic, P-1 |
| Unit cell dimensions | a = 9.6942(4) A alpha = 78.603(3) deg. |
| | b = 10.2573(4) A beta = 80.026(3) deg. |
| | c = 11.3475(5) A gamma = 77.116(3) deg. |
| Volume | 1068.37(8) A^3 |
| Z, Calculated density | 2, 1.230 Mg/m^3 |
| Absorption coefficient | 0.628 mm^-1 |
| F(000) | 428 |
| Crystal size | 0.240 x 0.160 x 0.120 mm |
| Theta range for data collection | 4.484 to 69.263 deg. |
| Limiting indices | -11<=h<=11, -12<=k<=12, -13<=l<=13 |
| Reflections collected / unique | 15820 / 3860 [R(int) = 0.0254] |
| Completeness to theta = 67.684 | 97.8 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00000 and 0.91230 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 3860 / 0 / 271 |
| Goodness-of-fit on F^2 | 1.159 |
| Final R indices [I>2sigma(I)] | R1 = 0.0496, wR2 = 0.1224 |
| R indices (all data) | R1 = 0.0502, wR2 = 0.1230 |
| Extinction coefficient | 0.081(3) |
| Largest diff. peak and hole | 0.367 and -0.432 e.A^-3 |

Table C.2s Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for ydpmp. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| N(1) | 8211(1) | 2293(1) | 4924(1) | 11(1) |
| O(1) | 6595(1) | -2098(1) | 8252(1) | 17(1) |
| O(2) | 6079(1) | 2956(1) | 4215(1) | 12(1) |
| O(3) | 6611(1) | 5712(1) | 5055(1) | 12(1) |
| C(1) | 5723(1) | -2895(1) | 7942(1) | 18(1) |
| C(2) | 6959(1) | -1058(1) | 7377(1) | 13(1) |
| C(3) | 7780(1) | -273(1) | 7711(1) | 16(1) |
| C(4) | 8182(1) | 819(1) | 6901(1) | 14(1) |
| C(5) | 7776(1) | 1145(1) | 5739(1) | 11(1) |
| C(6) | 6988(1) | 336(1) | 5400(1) | 12(1) |

| | | | | |
|---|---|---|---|---|
| C(7) | 6575(1) | -763(1) | 6212(1) | 13(1) |
| C(8) | 7275(1) | 3180(1) | 4241(1) | 10(1) |
| C(9) | 7699(1) | 4472(1) | 3440(1) | 10(1) |
| C(10) | 9167(1) | 4703(1) | 3591(1) | 12(1) |
| C(11) | 10226(1) | 3387(1) | 3883(1) | 13(1) |
| C(12) | 9618(1) | 2556(1) | 5029(1) | 14(1) |
| C(13) | 7615(1) | 4363(1) | 2115(1) | 12(1) |
| C(14) | 8642(1) | 3200(1) | 1578(1) | 12(1) |
| C(15) | 8307(1) | 3039(1) | 348(1) | 14(1) |
| C(16) | 8357(2) | 4320(1) | -594(1) | 20(1) |
| C(17) | 9337(2) | 1832(2) | -106(1) | 23(1) |
| C(18) | 6494(1) | 5657(1) | 3824(1) | 10(1) |
| C(19) | 6538(1) | 7022(1) | 3011(1) | 11(1) |
| C(20) | 7431(1) | 7831(1) | 3208(1) | 13(1) |
| C(21) | 7543(1) | 9066(1) | 2472(1) | 17(1) |
| C(22) | 6741(2) | 9518(1) | 1518(1) | 20(1) |
| C(23) | 5817(2) | 8747(1) | 1340(1) | 20(1) |
| C(24) | 5679(1) | 7507(1) | 2075(1) | 15(1) |
| C(25) | 4590(2) | 6779(1) | 1835(1) | 22(1) |

Table C.3s Bond lengths [A] and angles [deg] for ydpmp.

| | |
|---|---|
| N(1)-C(8) | 1.3593(15) |
| N(1)-C(5) | 1.4405(15) |
| N(1)-C(12) | 1.4767(15) |
| O(1)-C(2) | 1.3697(14) |
| O(1)-C(1) | 1.4255(15) |
| O(2)-C(8) | 1.2370(14) |
| O(3)-C(18) | 1.4331(13) |
| O(3)-H(3) | 0.88(2) |
| C(1)-H(1A) | 0.9800 |
| C(1)-H(1B) | 0.9800 |
| C(1)-H(1C) | 0.9800 |
| C(2)-C(3) | 1.3912(17) |
| C(2)-C(7) | 1.3928(17) |
| C(3)-C(4) | 1.3833(17) |
| C(3)-H(3A) | 0.9500 |
| C(4)-C(5) | 1.3969(17) |
| C(4)-H(4) | 0.9500 |
| C(5)-C(6) | 1.3899(17) |
| C(6)-C(7) | 1.3940(17) |
| C(6)-H(6) | 0.9500 |
| C(7)-H(7) | 0.9500 |
| C(8)-C(9) | 1.5455(15) |

| | |
|---|---|
| C(9)-C(10) | 1.5375(15) |
| C(9)-C(13) | 1.5468(15) |
| C(9)-C(18) | 1.5604(16) |
| C(10)-C(11) | 1.5195(17) |
| C(10)-H(10A) | 0.9900 |
| C(10)-H(10B) | 0.9900 |
| C(11)-C(12) | 1.5119(16) |
| C(11)-H(11A) | 0.9900 |
| C(11)-H(11B) | 0.9900 |
| C(12)-H(12A) | 0.9900 |
| C(12)-H(12B) | 0.9900 |
| C(13)-C(14) | 1.5276(17) |
| C(13)-H(13A) | 0.9900 |
| C(13)-H(13B) | 0.9900 |
| C(14)-C(15) | 1.5336(16) |
| C(14)-H(14A) | 0.9900 |
| C(14)-H(14B) | 0.9900 |
| C(15)-C(17) | 1.5229(18) |
| C(15)-C(16) | 1.5253(17) |
| C(15)-H(15) | 1.0000 |
| C(16)-H(16A) | 0.9800 |
| C(16)-H(16B) | 0.9800 |
| C(16)-H(16C) | 0.9800 |
| C(17)-H(17A) | 0.9800 |
| C(17)-H(17B) | 0.9800 |
| C(17)-H(17C) | 0.9800 |
| C(18)-C(19) | 1.5221(16) |
| C(18)-H(18) | 1.0000 |
| C(19)-C(20) | 1.3958(17) |
| C(19)-C(24) | 1.4077(17) |
| C(20)-C(21) | 1.3877(17) |
| C(20)-H(20) | 0.9500 |
| C(21)-C(22) | 1.387(2) |
| C(21)-H(21) | 0.9500 |
| C(22)-C(23) | 1.3820(19) |
| C(22)-H(22) | 0.9500 |
| C(23)-C(24) | 1.3960(18) |
| C(23)-H(23) | 0.9500 |
| C(24)-C(25) | 1.5087(17) |
| C(25)-H(25A) | 0.9800 |
| C(25)-H(25B) | 0.9800 |
| C(25)-H(25C) | 0.9800 |
| C(8)-N(1)-C(5) | 120.55(9) |
| C(8)-N(1)-C(12) | 122.71(10) |
| C(5)-N(1)-C(12) | 116.01(9) |
| C(2)-O(1)-C(1) | 116.70(9) |

| | |
|---|---|
| C(18)-O(3)-H(3) | 104.2(12) |
| O(1)-C(1)-H(1A) | 109.5 |
| O(1)-C(1)-H(1B) | 109.5 |
| H(1A)-C(1)-H(1B) | 109.5 |
| O(1)-C(1)-H(1C) | 109.5 |
| H(1A)-C(1)-H(1C) | 109.5 |
| H(1B)-C(1)-H(1C) | 109.5 |
| O(1)-C(2)-C(3) | 115.65(10) |
| O(1)-C(2)-C(7) | 124.63(11) |
| C(3)-C(2)-C(7) | 119.72(11) |
| C(4)-C(3)-C(2) | 120.23(11) |
| C(4)-C(3)-H(3A) | 119.9 |
| C(2)-C(3)-H(3A) | 119.9 |
| C(3)-C(4)-C(5) | 120.65(11) |
| C(3)-C(4)-H(4) | 119.7 |
| C(5)-C(4)-H(4) | 119.7 |
| C(6)-C(5)-C(4) | 118.85(11) |
| C(6)-C(5)-N(1) | 122.12(10) |
| C(4)-C(5)-N(1) | 119.01(10) |
| C(5)-C(6)-C(7) | 120.82(11) |
| C(5)-C(6)-H(6) | 119.6 |
| C(7)-C(6)-H(6) | 119.6 |
| C(2)-C(7)-C(6) | 119.69(11) |
| C(2)-C(7)-H(7) | 120.2 |
| C(6)-C(7)-H(7) | 120.2 |
| O(2)-C(8)-N(1) | 121.03(10) |
| O(2)-C(8)-C(9) | 118.21(10) |
| N(1)-C(8)-C(9) | 120.72(10) |
| C(10)-C(9)-C(8) | 114.25(9) |
| C(10)-C(9)-C(13) | 111.92(9) |
| C(8)-C(9)-C(13) | 106.64(9) |
| C(10)-C(9)-C(18) | 110.52(9) |
| C(8)-C(9)-C(18) | 104.67(9) |
| C(13)-C(9)-C(18) | 108.44(9) |
| C(11)-C(10)-C(9) | 112.80(9) |
| C(11)-C(10)-H(10A) | 109.0 |
| C(9)-C(10)-H(10A) | 109.0 |
| C(11)-C(10)-H(10B) | 109.0 |
| C(9)-C(10)-H(10B) | 109.0 |
| H(10A)-C(10)-H(10B) | 107.8 |
| C(12)-C(11)-C(10) | 109.14(10) |
| C(12)-C(11)-H(11A) | 109.9 |
| C(10)-C(11)-H(11A) | 109.9 |
| C(12)-C(11)-H(11B) | 109.9 |
| C(10)-C(11)-H(11B) | 109.9 |
| H(11A)-C(11)-H(11B) | 108.3 |

| | |
|---|---|
| N(1)-C(12)-C(11) | 111.81(9) |
| N(1)-C(12)-H(12A) | 109.3 |
| C(11)-C(12)-H(12A) | 109.3 |
| N(1)-C(12)-H(12B) | 109.3 |
| C(11)-C(12)-H(12B) | 109.3 |
| H(12A)-C(12)-H(12B) | 107.9 |
| C(14)-C(13)-C(9) | 117.28(10) |
| C(14)-C(13)-H(13A) | 108.0 |
| C(9)-C(13)-H(13A) | 108.0 |
| C(14)-C(13)-H(13B) | 108.0 |
| C(9)-C(13)-H(13B) | 108.0 |
| H(13A)-C(13)-H(13B) | 107.2 |
| C(13)-C(14)-C(15) | 113.00(10) |
| C(13)-C(14)-H(14A) | 109.0 |
| C(15)-C(14)-H(14A) | 109.0 |
| C(13)-C(14)-H(14B) | 109.0 |
| C(15)-C(14)-H(14B) | 109.0 |
| H(14A)-C(14)-H(14B) | 107.8 |
| C(17)-C(15)-C(16) | 110.43(11) |
| C(17)-C(15)-C(14) | 109.94(10) |
| C(16)-C(15)-C(14) | 112.17(10) |
| C(17)-C(15)-H(15) | 108.1 |
| C(16)-C(15)-H(15) | 108.1 |
| C(14)-C(15)-H(15) | 108.1 |
| C(15)-C(16)-H(16A) | 109.5 |
| C(15)-C(16)-H(16B) | 109.5 |
| H(16A)-C(16)-H(16B) | 109.5 |
| C(15)-C(16)-H(16C) | 109.5 |
| H(16A)-C(16)-H(16C) | 109.5 |
| H(16B)-C(16)-H(16C) | 109.5 |
| C(15)-C(17)-H(17A) | 109.5 |
| C(15)-C(17)-H(17B) | 109.5 |
| H(17A)-C(17)-H(17B) | 109.5 |
| C(15)-C(17)-H(17C) | 109.5 |
| H(17A)-C(17)-H(17C) | 109.5 |
| H(17B)-C(17)-H(17C) | 109.5 |
| O(3)-C(18)-C(19) | 111.56(9) |
| O(3)-C(18)-C(9) | 106.30(9) |
| C(19)-C(18)-C(9) | 114.50(9) |
| O(3)-C(18)-H(18) | 108.1 |
| C(19)-C(18)-H(18) | 108.1 |
| C(9)-C(18)-H(18) | 108.1 |
| C(20)-C(19)-C(24) | 118.84(11) |
| C(20)-C(19)-C(18) | 119.45(10) |
| C(24)-C(19)-C(18) | 121.70(10) |
| C(21)-C(20)-C(19) | 121.79(11) |

| | |
|---|---|
| C(21)-C(20)-H(20) | 119.1 |
| C(19)-C(20)-H(20) | 119.1 |
| C(22)-C(21)-C(20) | 119.34(12) |
| C(22)-C(21)-H(21) | 120.3 |
| C(20)-C(21)-H(21) | 120.3 |
| C(23)-C(22)-C(21) | 119.33(12) |
| C(23)-C(22)-H(22) | 120.3 |
| C(21)-C(22)-H(22) | 120.3 |
| C(22)-C(23)-C(24) | 122.29(12) |
| C(22)-C(23)-H(23) | 118.9 |
| C(24)-C(23)-H(23) | 118.9 |
| C(23)-C(24)-C(19) | 118.30(11) |
| C(23)-C(24)-C(25) | 117.88(11) |
| C(19)-C(24)-C(25) | 123.81(11) |
| C(24)-C(25)-H(25A) | 109.5 |
| C(24)-C(25)-H(25B) | 109.5 |
| H(25A)-C(25)-H(25B) | 109.5 |
| C(24)-C(25)-H(25C) | 109.5 |
| H(25A)-C(25)-H(25C) | 109.5 |
| H(25B)-C(25)-H(25C) | 109.5 |

Table C.4s Anisotropic displacement parameters (A^2 x 10^3) for ydpmp. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| N(1) | 10(1) | 10(1) | 13(1) | -1(1) | -4(1) | -1(1) |
| O(1) | 23(1) | 16(1) | 15(1) | 2(1) | -6(1) | -8(1) |
| O(2) | 9(1) | 12(1) | 15(1) | -2(1) | -3(1) | -1(1) |
| O(3) | 11(1) | 15(1) | 9(1) | -4(1) | -1(1) | 1(1) |
| C(1) | 20(1) | 17(1) | 20(1) | 0(1) | -5(1) | -8(1) |
| C(2) | 13(1) | 10(1) | 14(1) | -1(1) | -2(1) | 1(1) |
| C(3) | 18(1) | 16(1) | 13(1) | -2(1) | -7(1) | -2(1) |
| C(4) | 15(1) | 14(1) | 16(1) | -4(1) | -7(1) | -2(1) |
| C(5) | 10(1) | 9(1) | 13(1) | -2(1) | -2(1) | 2(1) |
| C(6) | 13(1) | 12(1) | 12(1) | -3(1) | -5(1) | 1(1) |
| C(7) | 12(1) | 12(1) | 17(1) | -5(1) | -5(1) | 0(1) |
| C(8) | 10(1) | 10(1) | 9(1) | -5(1) | -1(1) | 1(1) |
| C(9) | 10(1) | 10(1) | 10(1) | -2(1) | -2(1) | 0(1) |
| C(10) | 10(1) | 13(1) | 12(1) | -3(1) | -2(1) | -2(1) |
| C(11) | 8(1) | 15(1) | 16(1) | -5(1) | -3(1) | 0(1) |
| C(12) | 10(1) | 14(1) | 18(1) | -2(1) | -6(1) | -1(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(13) | 13(1) | 12(1) | 10(1) | -2(1) | -3(1) | -1(1) |
| C(14) | 13(1) | 12(1) | 11(1) | -3(1) | -2(1) | -1(1) |
| C(15) | 14(1) | 17(1) | 12(1) | -5(1) | -2(1) | -3(1) |
| C(16) | 27(1) | 23(1) | 12(1) | -1(1) | -4(1) | -5(1) |
| C(17) | 26(1) | 25(1) | 19(1) | -12(1) | -5(1) | 2(1) |
| C(18) | 10(1) | 12(1) | 9(1) | -3(1) | -2(1) | -1(1) |
| C(19) | 10(1) | 10(1) | 11(1) | -4(1) | 0(1) | 2(1) |
| C(20) | 12(1) | 14(1) | 14(1) | -4(1) | -1(1) | 0(1) |
| C(21) | 16(1) | 14(1) | 21(1) | -6(1) | 2(1) | -4(1) |
| C(22) | 25(1) | 12(1) | 18(1) | 1(1) | 1(1) | 0(1) |
| C(23) | 25(1) | 15(1) | 17(1) | -1(1) | -8(1) | 3(1) |
| C(24) | 17(1) | 13(1) | 15(1) | -5(1) | -5(1) | 2(1) |
| C(25) | 24(1) | 16(1) | 29(1) | -4(1) | -18(1) | 2(1) |

Table C.5s Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for ydpmp.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(3) | 5780(20) | 6179(19) | 5323(17) | 28(4) |
| H(1A) | 4859 | -2302 | 7663 | 27 |
| H(1B) | 5455 | -3545 | 8657 | 27 |
| H(1C) | 6255 | -3387 | 7294 | 27 |
| H(3A) | 8066 | -487 | 8497 | 19 |
| H(4) | 8740 | 1351 | 7138 | 17 |
| H(6) | 6728 | 535 | 4605 | 15 |
| H(7) | 6034 | -1308 | 5972 | 16 |
| H(10A) | 9560 | 5239 | 2833 | 14 |
| H(10B) | 9047 | 5239 | 4251 | 14 |
| H(11A) | 10409 | 2870 | 3203 | 16 |
| H(11B) | 11143 | 3586 | 3997 | 16 |
| H(12A) | 10288 | 1681 | 5201 | 16 |
| H(12B) | 9520 | 3045 | 5718 | 16 |
| H(13A) | 6629 | 4281 | 2065 | 14 |
| H(13B) | 7781 | 5224 | 1594 | 14 |
| H(14A) | 8599 | 2344 | 2153 | 15 |
| H(14B) | 9629 | 3362 | 1477 | 15 |
| H(15) | 7318 | 2852 | 468 | 16 |
| H(16A) | 9308 | 4543 | -703 | 31 |
| H(16B) | 7639 | 5073 | -316 | 31 |
| H(16C) | 8157 | 4167 | -1368 | 31 |
| H(17A) | 9058 | 1680 | -850 | 34 |
| H(17B) | 9309 | 1021 | 516 | 34 |

| | | | | |
|---|---|---|---|---|
| H(17C) | 10308 | 2016 | -275 | 34 |
| H(18) | 5553 | 5416 | 3811 | 12 |
| H(20) | 7977 | 7528 | 3864 | 16 |
| H(21) | 8164 | 9596 | 2619 | 20 |
| H(22) | 6825 | 10349 | 993 | 24 |
| H(23) | 5256 | 9072 | 696 | 24 |
| H(25A) | 3875 | 7429 | 1392 | 33 |
| H(25B) | 4121 | 6361 | 2609 | 33 |
| H(25C) | 5068 | 6074 | 1350 | 33 |

Table C.6s Torsion angles [deg] for ydpmp.

| | |
|---|---|
| C(1)-O(1)-C(2)-C(3) | 178.45(11) |
| C(1)-O(1)-C(2)-C(7) | -2.14(17) |
| O(1)-C(2)-C(3)-C(4) | -178.80(11) |
| C(7)-C(2)-C(3)-C(4) | 1.76(19) |
| C(2)-C(3)-C(4)-C(5) | -0.25(19) |
| C(3)-C(4)-C(5)-C(6) | -1.45(19) |
| C(3)-C(4)-C(5)-N(1) | 179.72(11) |
| C(8)-N(1)-C(5)-C(6) | 44.60(16) |
| C(12)-N(1)-C(5)-C(6) | -144.90(11) |
| C(8)-N(1)-C(5)-C(4) | -136.60(12) |
| C(12)-N(1)-C(5)-C(4) | 33.89(15) |
| C(4)-C(5)-C(6)-C(7) | 1.66(18) |
| N(1)-C(5)-C(6)-C(7) | -179.55(10) |
| O(1)-C(2)-C(7)-C(6) | 179.07(11) |
| C(3)-C(2)-C(7)-C(6) | -1.55(18) |
| C(5)-C(6)-C(7)-C(2) | -0.17(18) |
| C(5)-N(1)-C(8)-O(2) | -6.98(16) |
| C(12)-N(1)-C(8)-O(2) | -176.82(10) |
| C(5)-N(1)-C(8)-C(9) | 175.28(10) |
| C(12)-N(1)-C(8)-C(9) | 5.44(16) |
| O(2)-C(8)-C(9)-C(10) | 176.63(10) |
| N(1)-C(8)-C(9)-C(10) | -5.57(15) |
| O(2)-C(8)-C(9)-C(13) | -59.18(13) |
| N(1)-C(8)-C(9)-C(13) | 118.62(11) |
| O(2)-C(8)-C(9)-C(18) | 55.61(13) |
| N(1)-C(8)-C(9)-C(18) | -126.58(11) |
| C(8)-C(9)-C(10)-C(11) | 32.18(13) |
| C(13)-C(9)-C(10)-C(11) | -89.14(12) |
| C(18)-C(9)-C(10)-C(11) | 149.90(10) |
| C(9)-C(10)-C(11)-C(12) | -57.76(12) |
| C(8)-N(1)-C(12)-C(11) | -31.54(15) |
| C(5)-N(1)-C(12)-C(11) | 158.19(10) |

| | |
|---|---|
| C(10)-C(11)-C(12)-N(1) | 56.52(13) |
| C(10)-C(9)-C(13)-C(14) | 61.78(13) |
| C(8)-C(9)-C(13)-C(14) | -63.83(12) |
| C(18)-C(9)-C(13)-C(14) | -176.06(9) |
| C(9)-C(13)-C(14)-C(15) | 170.33(10) |
| C(13)-C(14)-C(15)-C(17) | -177.88(10) |
| C(13)-C(14)-C(15)-C(16) | 58.83(13) |
| C(10)-C(9)-C(18)-O(3) | -57.30(11) |
| C(8)-C(9)-C(18)-O(3) | 66.16(10) |
| C(13)-C(9)-C(18)-O(3) | 179.69(8) |
| C(10)-C(9)-C(18)-C(19) | 66.35(12) |
| C(8)-C(9)-C(18)-C(19) | -170.19(9) |
| C(13)-C(9)-C(18)-C(19) | -56.66(12) |
| O(3)-C(18)-C(19)-C(20) | 36.92(14) |
| C(9)-C(18)-C(19)-C(20) | -83.87(13) |
| O(3)-C(18)-C(19)-C(24) | -141.76(11) |
| C(9)-C(18)-C(19)-C(24) | 97.46(13) |
| C(24)-C(19)-C(20)-C(21) | -3.15(18) |
| C(18)-C(19)-C(20)-C(21) | 178.14(11) |
| C(19)-C(20)-C(21)-C(22) | 0.50(19) |
| C(20)-C(21)-C(22)-C(23) | 1.7(2) |
| C(21)-C(22)-C(23)-C(24) | -1.3(2) |
| C(22)-C(23)-C(24)-C(19) | -1.4(2) |
| C(22)-C(23)-C(24)-C(25) | 177.32(12) |
| C(20)-C(19)-C(24)-C(23) | 3.51(18) |
| C(18)-C(19)-C(24)-C(23) | -177.81(11) |
| C(20)-C(19)-C(24)-C(25) | -175.10(12) |
| C(18)-C(19)-C(24)-C(25) | 3.58(19) |

Table C.7s Hydrogen bonds for ydpmp [A and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(3)-H(3)...O(2)#1 | 0.88(2) | 1.86(2) | 2.7318(12) | 172.7(17) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

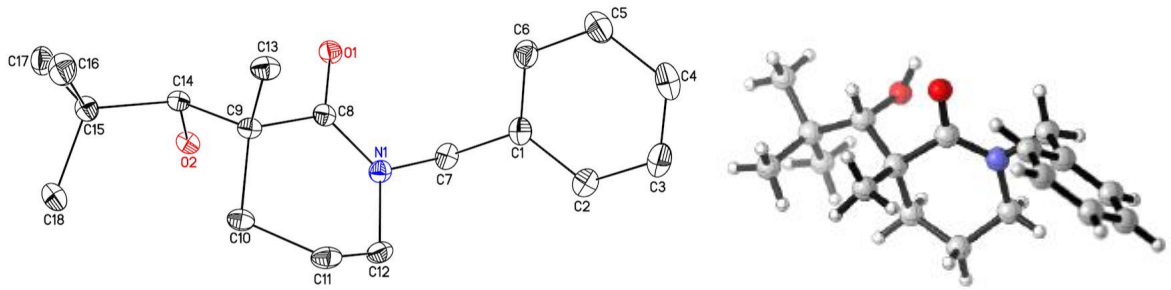


Figure C.20 Structure of yd3me.

**Structure Determination.**

Colorless blocks of **yd3me** were grown from a dichloromethane/hexanes solution of the compound at 22 deg. C. A crystal of dimensions 0.28 x 0.18 x 0.14 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (ë = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ù. The exposure times were 1 sec. for the low angle images, 3 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 23791 reflections to a maximum 2è value of 138.41° of which 2997 were independent and 2975 were greater than 2ó(I). The final cell constants (Table 1) were based on the xyz centroids 20289 reflections above 10ó(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group P2(1)/n with Z = 4 for the formula $C_{18}H_{27}NO_2$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in a mix of idealized and refined positions. Full matrix least-squares refinement based on $F^2$ converged at R1 = 0.0533 and wR2 = 0.1197 [based on I > 2sigma(I)], R1 = 0.0534 and wR2 = 0.1198 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Sheldrick, G.M. SHELXTL, v. 2014/6; Bruker Analytical X-ray, Madison, WI, 2014.
CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.
CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015).

Table C.1t Crystal data and structure refinement for yd3me.

| | |
|---|---|
| Identification code | yd3me |
| Empirical formula | C18 H27 N O2 |
| Formula weight | 289.40 |
| Temperature | 85(2) K |
| Wavelength | 1.54184 A |
| Crystal system, space group | Monoclinic, P2(1)/n |
| Unit cell dimensions | a = 11.87390(10) A alpha = 90 deg. |
| | b = 6.82896(3) A beta = 93.2860(10) deg. |

| | |
|---|---|
| | c = 20.03490(10) A gamma = 90 deg. |
| Volume | 1621.887(17) A^3 |
| Z, Calculated density | 4, 1.185 Mg/m^3 |
| Absorption coefficient | 0.596 mm^-1 |
| F(000) | 632 |
| Crystal size | 0.280 x 0.180 x 0.140 mm |
| Theta range for data collection | 6.851 to 69.203 deg. |
| Limiting indices | -14<=h<=13, -8<=k<=8, -24<=l<=21 |
| Reflections collected / unique | 23791 / 2997 [R(int) = 0.0353] |
| Completeness to theta = 67.684 | 99.5 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00000 and 0.87795 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 2997 / 0 / 199 |
| Goodness-of-fit on F^2 | 1.221 |
| Final R indices [I>2sigma(I)] | R1 = 0.0533, wR2 = 0.1197 |
| R indices (all data) | R1 = 0.0534, wR2 = 0.1198 |
| Extinction coefficient | 0.071(3) |
| Largest diff. peak and hole | 0.310 and -0.450 e.A^-3 |

Table C.2t Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for yd3me. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| N(1) | 4492(1) | 8736(2) | 5845(1) | 15(1) |
| O(1) | 4737(1) | 5461(1) | 5767(1) | 16(1) |
| O(2) | 6843(1) | 6639(1) | 5098(1) | 14(1) |
| C(1) | 2505(1) | 8610(2) | 6144(1) | 17(1) |
| C(2) | 1845(1) | 10249(2) | 6255(1) | 20(1) |
| C(3) | 1130(1) | 10271(2) | 6783(1) | 24(1) |
| C(4) | 1074(1) | 8663(2) | 7200(1) | 24(1) |
| C(5) | 1725(1) | 7020(2) | 7090(1) | 23(1) |
| C(6) | 2436(1) | 6990(2) | 6564(1) | 21(1) |
| C(7) | 3311(1) | 8598(2) | 5584(1) | 17(1) |
| C(8) | 5122(1) | 7104(2) | 5917(1) | 13(1) |
| C(9) | 6340(1) | 7243(2) | 6234(1) | 13(1) |
| C(10) | 6764(1) | 9362(2) | 6289(1) | 15(1) |
| C(11) | 5854(1) | 10726(2) | 6521(1) | 18(1) |
| C(12) | 4871(1) | 10736(2) | 6009(1) | 17(1) |
| C(13) | 6237(1) | 6381(2) | 6943(1) | 17(1) |
| C(14) | 7056(1) | 5958(2) | 5773(1) | 12(1) |
| C(15) | 8360(1) | 5797(2) | 5897(1) | 16(1) |
| C(16) | 8711(1) | 5299(2) | 6625(1) | 22(1) |

| | | | | |
|---|---|---|---|---|
| C(17) | 8737(1) | 4087(2) | 5463(1) | 21(1) |
| C(18) | 9003(1) | 7635(2) | 5691(1) | 19(1) |

Table C.3t Bond lengths [A] and angles [deg] for yd3me.

| | |
|---|---|
| N(1)-C(8) | 1.3461(16) |
| N(1)-C(12) | 1.4697(16) |
| N(1)-C(7) | 1.4707(15) |
| O(1)-C(8) | 1.2419(15) |
| O(2)-C(14) | 1.4386(14) |
| O(2)-H(2) | 0.88(2) |
| C(1)-C(2) | 1.3922(18) |
| C(1)-C(6) | 1.3954(18) |
| C(1)-C(7) | 1.5148(16) |
| C(2)-C(3) | 1.3932(19) |
| C(2)-H(2A) | 0.9500 |
| C(3)-C(4) | 1.383(2) |
| C(3)-H(3) | 0.9500 |
| C(4)-C(5) | 1.387(2) |
| C(4)-H(4) | 0.9500 |
| C(5)-C(6) | 1.3880(18) |
| C(5)-H(5) | 0.9500 |
| C(6)-H(6) | 0.9500 |
| C(7)-H(7A) | 0.9900 |
| C(7)-H(7B) | 0.9900 |
| C(8)-C(9) | 1.5477(16) |
| C(9)-C(10) | 1.5344(15) |
| C(9)-C(13) | 1.5490(15) |
| C(9)-C(14) | 1.5614(15) |
| C(10)-C(11) | 1.5198(17) |
| C(10)-H(10A) | 0.9900 |
| C(10)-H(10B) | 0.9900 |
| C(11)-C(12) | 1.5095(17) |
| C(11)-H(11A) | 0.9900 |
| C(11)-H(11B) | 0.9900 |
| C(12)-H(12A) | 0.9900 |
| C(12)-H(12B) | 0.9900 |
| C(13)-H(13A) | 0.9800 |
| C(13)-H(13B) | 0.9800 |
| C(13)-H(13C) | 0.9800 |
| C(14)-C(15) | 1.5581(15) |
| C(14)-H(14) | 1.0000 |
| C(15)-C(16) | 1.5315(17) |
| C(15)-C(18) | 1.5371(17) |

| | |
|---|---|
| C(15)-C(17) | 1.5375(17) |
| C(16)-H(16A) | 0.9800 |
| C(16)-H(16B) | 0.9800 |
| C(16)-H(16C) | 0.9800 |
| C(17)-H(17A) | 0.9800 |
| C(17)-H(17B) | 0.9800 |
| C(17)-H(17C) | 0.9800 |
| C(18)-H(18A) | 0.9800 |
| C(18)-H(18B) | 0.9800 |
| C(18)-H(18C) | 0.9800 |
| C(8)-N(1)-C(12) | 125.74(10) |
| C(8)-N(1)-C(7) | 119.87(10) |
| C(12)-N(1)-C(7) | 114.38(9) |
| C(14)-O(2)-H(2) | 109.0(13) |
| C(2)-C(1)-C(6) | 119.15(12) |
| C(2)-C(1)-C(7) | 120.58(11) |
| C(6)-C(1)-C(7) | 120.25(11) |
| C(1)-C(2)-C(3) | 120.27(12) |
| C(1)-C(2)-H(2A) | 119.9 |
| C(3)-C(2)-H(2A) | 119.9 |
| C(4)-C(3)-C(2) | 120.13(12) |
| C(4)-C(3)-H(3) | 119.9 |
| C(2)-C(3)-H(3) | 119.9 |
| C(3)-C(4)-C(5) | 119.97(12) |
| C(3)-C(4)-H(4) | 120.0 |
| C(5)-C(4)-H(4) | 120.0 |
| C(4)-C(5)-C(6) | 120.10(12) |
| C(4)-C(5)-H(5) | 119.9 |
| C(6)-C(5)-H(5) | 119.9 |
| C(5)-C(6)-C(1) | 120.38(12) |
| C(5)-C(6)-H(6) | 119.8 |
| C(1)-C(6)-H(6) | 119.8 |
| N(1)-C(7)-C(1) | 111.48(9) |
| N(1)-C(7)-H(7A) | 109.3 |
| C(1)-C(7)-H(7A) | 109.3 |
| N(1)-C(7)-H(7B) | 109.3 |
| C(1)-C(7)-H(7B) | 109.3 |
| H(7A)-C(7)-H(7B) | 108.0 |
| O(1)-C(8)-N(1) | 121.81(11) |
| O(1)-C(8)-C(9) | 118.50(10) |
| N(1)-C(8)-C(9) | 119.59(10) |
| C(10)-C(9)-C(8) | 112.48(9) |
| C(10)-C(9)-C(13) | 109.60(9) |
| C(8)-C(9)-C(13) | 103.41(9) |
| C(10)-C(9)-C(14) | 112.64(9) |
| C(8)-C(9)-C(14) | 104.50(9) |

| | |
|---|---|
| C(13)-C(9)-C(14) | 113.80(9) |
| C(11)-C(10)-C(9) | 111.32(9) |
| C(11)-C(10)-H(10A) | 109.4 |
| C(9)-C(10)-H(10A) | 109.4 |
| C(11)-C(10)-H(10B) | 109.4 |
| C(9)-C(10)-H(10B) | 109.4 |
| H(10A)-C(10)-H(10B) | 108.0 |
| C(12)-C(11)-C(10) | 109.25(10) |
| C(12)-C(11)-H(11A) | 109.8 |
| C(10)-C(11)-H(11A) | 109.8 |
| C(12)-C(11)-H(11B) | 109.8 |
| C(10)-C(11)-H(11B) | 109.8 |
| H(11A)-C(11)-H(11B) | 108.3 |
| N(1)-C(12)-C(11) | 111.26(10) |
| N(1)-C(12)-H(12A) | 109.4 |
| C(11)-C(12)-H(12A) | 109.4 |
| N(1)-C(12)-H(12B) | 109.4 |
| C(11)-C(12)-H(12B) | 109.4 |
| H(12A)-C(12)-H(12B) | 108.0 |
| C(9)-C(13)-H(13A) | 109.5 |
| C(9)-C(13)-H(13B) | 109.5 |
| H(13A)-C(13)-H(13B) | 109.5 |
| C(9)-C(13)-H(13C) | 109.5 |
| H(13A)-C(13)-H(13C) | 109.5 |
| H(13B)-C(13)-H(13C) | 109.5 |
| O(2)-C(14)-C(15) | 107.00(9) |
| O(2)-C(14)-C(9) | 107.56(9) |
| C(15)-C(14)-C(9) | 121.03(9) |
| O(2)-C(14)-H(14) | 106.8 |
| C(15)-C(14)-H(14) | 106.8 |
| C(9)-C(14)-H(14) | 106.8 |
| C(16)-C(15)-C(18) | 108.94(10) |
| C(16)-C(15)-C(17) | 107.29(10) |
| C(18)-C(15)-C(17) | 107.69(10) |
| C(16)-C(15)-C(14) | 112.39(10) |
| C(18)-C(15)-C(14) | 113.82(10) |
| C(17)-C(15)-C(14) | 106.37(9) |
| C(15)-C(16)-H(16A) | 109.5 |
| C(15)-C(16)-H(16B) | 109.5 |
| H(16A)-C(16)-H(16B) | 109.5 |
| C(15)-C(16)-H(16C) | 109.5 |
| H(16A)-C(16)-H(16C) | 109.5 |
| H(16B)-C(16)-H(16C) | 109.5 |
| C(15)-C(17)-H(17A) | 109.5 |
| C(15)-C(17)-H(17B) | 109.5 |
| H(17A)-C(17)-H(17B) | 109.5 |

| | |
|---|---|
| C(15)-C(17)-H(17C) | 109.5 |
| H(17A)-C(17)-H(17C) | 109.5 |
| H(17B)-C(17)-H(17C) | 109.5 |
| C(15)-C(18)-H(18A) | 109.5 |
| C(15)-C(18)-H(18B) | 109.5 |
| H(18A)-C(18)-H(18B) | 109.5 |
| C(15)-C(18)-H(18C) | 109.5 |
| H(18A)-C(18)-H(18C) | 109.5 |
| H(18B)-C(18)-H(18C) | 109.5 |

Table C.4t Anisotropic displacement parameters (A^2 x 10^3) for yd3me. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| N(1) | 17(1) | 14(1) | 13(1) | -1(1) | 2(1) | 0(1) |
| O(1) | 16(1) | 14(1) | 20(1) | -4(1) | 2(1) | -2(1) |
| O(2) | 17(1) | 17(1) | 9(1) | 0(1) | 0(1) | -3(1) |
| C(1) | 14(1) | 22(1) | 14(1) | -2(1) | -2(1) | 1(1) |
| C(2) | 20(1) | 21(1) | 18(1) | -2(1) | -1(1) | 2(1) |
| C(3) | 19(1) | 28(1) | 25(1) | -7(1) | 1(1) | 4(1) |
| C(4) | 16(1) | 37(1) | 20(1) | -5(1) | 3(1) | -2(1) |
| C(5) | 18(1) | 30(1) | 22(1) | 5(1) | 1(1) | -2(1) |
| C(6) | 17(1) | 23(1) | 22(1) | 2(1) | 1(1) | 4(1) |
| C(7) | 18(1) | 21(1) | 12(1) | -1(1) | -1(1) | 3(1) |
| C(8) | 17(1) | 14(1) | 9(1) | -2(1) | 4(1) | -1(1) |
| C(9) | 16(1) | 12(1) | 10(1) | -1(1) | 1(1) | -1(1) |
| C(10) | 19(1) | 13(1) | 14(1) | -1(1) | 0(1) | -3(1) |
| C(11) | 26(1) | 12(1) | 15(1) | -3(1) | 2(1) | -3(1) |
| C(12) | 23(1) | 12(1) | 18(1) | -1(1) | 4(1) | 1(1) |
| C(13) | 24(1) | 15(1) | 12(1) | 0(1) | 3(1) | -1(1) |
| C(14) | 15(1) | 12(1) | 9(1) | 0(1) | 1(1) | -1(1) |
| C(15) | 15(1) | 19(1) | 14(1) | 1(1) | 0(1) | -1(1) |
| C(16) | 19(1) | 29(1) | 18(1) | 5(1) | -2(1) | 1(1) |
| C(17) | 16(1) | 23(1) | 25(1) | -3(1) | 3(1) | 2(1) |
| C(18) | 16(1) | 24(1) | 19(1) | 1(1) | 1(1) | -4(1) |

Table C.5t Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for yd3me.

| | x | y | z | U(eq) |
|---|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| H(2) | 6298(17) | 5930(30) | 4902(10) | 37(5) |
| H(2A) | 1881 | 11356 | 5971 | 24 |
| H(3) | 681 | 11393 | 6857 | 29 |
| H(4) | 589 | 8684 | 7561 | 29 |
| H(5) | 1684 | 5915 | 7375 | 28 |
| H(6) | 2878 | 5860 | 6490 | 25 |
| H(7A) | 3206 | 7376 | 5322 | 21 |
| H(7B) | 3136 | 9715 | 5281 | 21 |
| H(10A) | 7430 | 9422 | 6609 | 18 |
| H(10B) | 7001 | 9803 | 5848 | 18 |
| H(11A) | 5599 | 10276 | 6958 | 21 |
| H(11B) | 6160 | 12067 | 6579 | 21 |
| H(12A) | 4240 | 11487 | 6185 | 21 |
| H(12B) | 5098 | 11396 | 5598 | 21 |
| H(13A) | 6930 | 6650 | 7216 | 25 |
| H(13B) | 6119 | 4963 | 6911 | 25 |
| H(13C) | 5595 | 6986 | 7151 | 25 |
| H(14) | 6749 | 4596 | 5791 | 15 |
| H(16A) | 9516 | 4974 | 6662 | 33 |
| H(16B) | 8272 | 4176 | 6768 | 33 |
| H(16C) | 8570 | 6429 | 6910 | 33 |
| H(17A) | 9558 | 3939 | 5519 | 32 |
| H(17B) | 8520 | 4354 | 4993 | 32 |
| H(17C) | 8372 | 2877 | 5602 | 32 |
| H(18A) | 8852 | 8711 | 5997 | 29 |
| H(18B) | 8752 | 8007 | 5234 | 29 |
| H(18C) | 9814 | 7358 | 5711 | 29 |

Table C.6t Torsion angles [deg] for yd3me.

| | |
|---|---|
| C(6)-C(1)-C(2)-C(3) | 0.41(18) |
| C(7)-C(1)-C(2)-C(3) | -178.07(11) |
| C(1)-C(2)-C(3)-C(4) | 0.04(19) |
| C(2)-C(3)-C(4)-C(5) | -0.4(2) |
| C(3)-C(4)-C(5)-C(6) | 0.22(19) |
| C(4)-C(5)-C(6)-C(1) | 0.23(19) |
| C(2)-C(1)-C(6)-C(5) | -0.55(18) |
| C(7)-C(1)-C(6)-C(5) | 177.94(11) |
| C(8)-N(1)-C(7)-C(1) | 98.13(12) |
| C(12)-N(1)-C(7)-C(1) | -81.69(12) |
| C(2)-C(1)-C(7)-N(1) | 107.37(12) |
| C(6)-C(1)-C(7)-N(1) | -71.10(14) |

| | |
|---|---|
| C(12)-N(1)-C(8)-O(1) | 179.92(10) |
| C(7)-N(1)-C(8)-O(1) | 0.12(16) |
| C(12)-N(1)-C(8)-C(9) | 3.69(17) |
| C(7)-N(1)-C(8)-C(9) | -176.11(9) |
| O(1)-C(8)-C(9)-C(10) | 170.94(10) |
| N(1)-C(8)-C(9)-C(10) | -12.71(14) |
| O(1)-C(8)-C(9)-C(13) | -70.90(12) |
| N(1)-C(8)-C(9)-C(13) | 105.45(11) |
| O(1)-C(8)-C(9)-C(14) | 48.44(13) |
| N(1)-C(8)-C(9)-C(14) | -135.20(10) |
| C(8)-C(9)-C(10)-C(11) | 42.05(13) |
| C(13)-C(9)-C(10)-C(11) | -72.40(12) |
| C(14)-C(9)-C(10)-C(11) | 159.83(9) |
| C(9)-C(10)-C(11)-C(12) | -62.81(12) |
| C(8)-N(1)-C(12)-C(11) | -23.79(16) |
| C(7)-N(1)-C(12)-C(11) | 156.02(10) |
| C(10)-C(11)-C(12)-N(1) | 51.89(13) |
| C(10)-C(9)-C(14)-O(2) | -69.07(11) |
| C(8)-C(9)-C(14)-O(2) | 53.33(11) |
| C(13)-C(9)-C(14)-O(2) | 165.41(9) |
| C(10)-C(9)-C(14)-C(15) | 54.18(14) |
| C(8)-C(9)-C(14)-C(15) | 176.58(10) |
| C(13)-C(9)-C(14)-C(15) | -71.34(13) |
| O(2)-C(14)-C(15)-C(16) | 173.72(10) |
| C(9)-C(14)-C(15)-C(16) | 50.20(14) |
| O(2)-C(14)-C(15)-C(18) | 49.26(12) |
| C(9)-C(14)-C(15)-C(18) | -74.25(13) |
| O(2)-C(14)-C(15)-C(17) | -69.15(11) |
| C(9)-C(14)-C(15)-C(17) | 167.33(10) |

Table C.7t Hydrogen bonds for yd3me [A and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(2)-H(2)...O(1)#1 | 0.88(2) | 2.01(2) | 2.8651(12) | 164.4(18) |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1

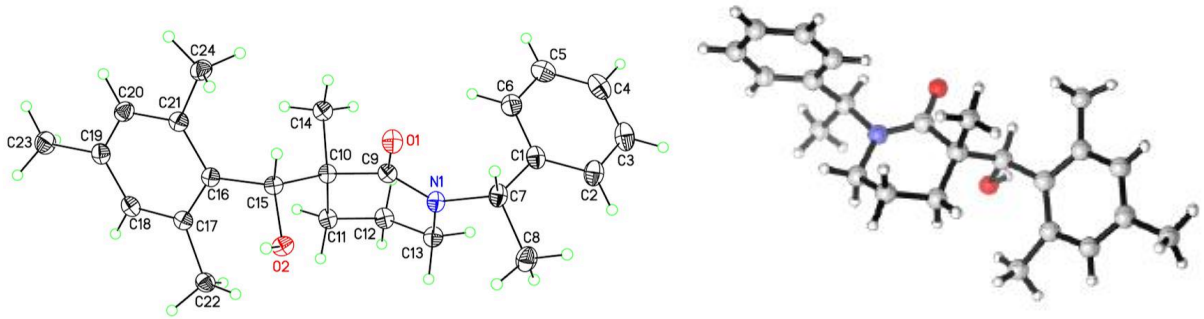



Figure C.21 Structure of nasymes.

**Structure Determination.**

Colorless blocks of **nasymes** were grown from a dichloromethane/hexanes solution of the compound at 22 deg. C. A crystal of dimensions 0.16 x 0.12 x 0.12 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (ë = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ù. The exposure times were 1 sec. for the low angle images, 3 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 29433 reflections to a maximum 2è value of 138.65° of which 3675 were independent and 3623 were greater than 2ó(I). The final cell constants (Table 1) were based on the xyz centroids 18479 reflections above 10ó(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group P2(1)/c with Z = 4 for the formula $C_{24}H_{31}NO_2$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in mix of idealized and refined positions. Full matrix least-squares refinement based on $F^2$ converged at R1 = 0.0432 and wR2 = 0.1082 [based on I > 2sigma(I)], R1 = 0.0435 and wR2 = 0.1085 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Sheldrick, G.M. SHELXTL, v. 2014/6; Bruker Analytical X-ray, Madison, WI, 2014.
CrystalClear Expert 2.0 r16, Rigaku Americas and Rigku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.
CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015).

Table C.1u Crystal data and structure refinement for nasymes.

| | |
|---|---|
| Identification code | nasymes |
| Empirical formula | C24 H31 N O2 |
| Formula weight | 365.50 |
| Temperature | 85(2) K |
| Wavelength | 1.54184 A |
| Crystal system, space group | Monoclinic, P2(1)/c |

| | |
|---|---|
| Unit cell dimensions | a = 11.15392(7) A alpha = 90 deg. |
| | b = 14.10357(12) A beta = 104.1061(7) deg. |
| | c = 13.03642(11) A gamma = 90 deg. |
| Volume | 1988.92(3) A^3 |
| Z, Calculated density | 4, 1.221 Mg/m^3 |
| Absorption coefficient | 0.595 mm^-1 |
| F(000) | 792 |
| Crystal size | 0.160 x 0.120 x 0.120 mm |
| Theta range for data collection | 4.697 to 69.323 deg. |
| Limiting indices | -13<=h<=13, -16<=k<=17, -15<=l<=15 |
| Reflections collected / unique | 29433 / 3675 [R(int) = 0.0512] |
| Completeness to theta = 67.684 | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00000 and 0.80251 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 3675 / 0 / 254 |
| Goodness-of-fit on F^2 | 1.059 |
| Final R indices [I>2sigma(I)] | R1 = 0.0432, wR2 = 0.1082 |
| R indices (all data) | R1 = 0.0435, wR2 = 0.1085 |
| Extinction coefficient | 0.0122(8) |
| Largest diff. peak and hole | 0.252 and -0.339 e.A^-3 |

Table C.2u Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for nasymes. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| N(1) | 8399(1) | 5995(1) | 7083(1) | 17(1) |
| O(1) | 9545(1) | 4852(1) | 6571(1) | 20(1) |
| O(2) | 8649(1) | 5887(1) | 4314(1) | 18(1) |
| C(1) | 8835(1) | 5795(1) | 9005(1) | 20(1) |
| C(2) | 8963(1) | 6313(1) | 9937(1) | 25(1) |
| C(3) | 8549(1) | 5942(1) | 10779(1) | 28(1) |
| C(4) | 7985(1) | 5066(1) | 10700(1) | 27(1) |
| C(5) | 7830(1) | 4550(1) | 9768(1) | 27(1) |
| C(6) | 8262(1) | 4913(1) | 8935(1) | 23(1) |
| C(7) | 9346(1) | 6139(1) | 8084(1) | 19(1) |
| C(8) | 9810(1) | 7159(1) | 8183(1) | 25(1) |
| C(9) | 8582(1) | 5327(1) | 6395(1) | 16(1) |
| C(10) | 7525(1) | 5090(1) | 5422(1) | 15(1) |
| C(11) | 6491(1) | 5834(1) | 5220(1) | 18(1) |
| C(12) | 6171(1) | 6139(1) | 6239(1) | 19(1) |
| C(13) | 7298(1) | 6600(1) | 6941(1) | 20(1) |
| C(14) | 7031(1) | 4123(1) | 5686(1) | 19(1) |

| | | | | |
|---|---|---|---|---|
| C(15) | 8111(1) | 4991(1) | 4459(1) | 15(1) |
| C(16) | 7233(1) | 4601(1) | 3451(1) | 16(1) |
| C(17) | 6345(1) | 5148(1) | 2734(1) | 16(1) |
| C(18) | 5550(1) | 4703(1) | 1870(1) | 18(1) |
| C(19) | 5622(1) | 3747(1) | 1653(1) | 20(1) |
| C(20) | 6544(1) | 3224(1) | 2331(1) | 20(1) |
| C(21) | 7343(1) | 3629(1) | 3214(1) | 18(1) |
| C(22) | 6198(1) | 6214(1) | 2775(1) | 20(1) |
| C(23) | 4771(1) | 3307(1) | 692(1) | 27(1) |
| C(24) | 8336(1) | 2994(1) | 3866(1) | 22(1) |

Table C.3u Bond lengths [A] and angles [deg] for nasymes.

| | |
|---|---|
| N(1)-C(9) | 1.3502(15) |
| N(1)-C(13) | 1.4695(15) |
| N(1)-C(7) | 1.4788(14) |
| O(1)-C(9) | 1.2396(14) |
| O(2)-C(15) | 1.4314(14) |
| O(2)-H(2) | 0.86(2) |
| C(1)-C(6) | 1.3923(19) |
| C(1)-C(2) | 1.3938(18) |
| C(1)-C(7) | 1.5284(17) |
| C(2)-C(3) | 1.393(2) |
| C(2)-H(2A) | 0.9500 |
| C(3)-C(4) | 1.380(2) |
| C(3)-H(3) | 0.9500 |
| C(4)-C(5) | 1.391(2) |
| C(4)-H(4) | 0.9500 |
| C(5)-C(6) | 1.3888(19) |
| C(5)-H(5) | 0.9500 |
| C(6)-H(6) | 0.9500 |
| C(7)-C(8) | 1.5233(18) |
| C(7)-H(7) | 1.0000 |
| C(8)-H(8A) | 0.9800 |
| C(8)-H(8B) | 0.9800 |
| C(8)-H(8C) | 0.9800 |
| C(9)-C(10) | 1.5427(15) |
| C(10)-C(11) | 1.5326(15) |
| C(10)-C(14) | 1.5417(16) |
| C(10)-C(15) | 1.5571(15) |
| C(11)-C(12) | 1.5192(16) |
| C(11)-H(11A) | 0.9900 |
| C(11)-H(11B) | 0.9900 |
| C(12)-C(13) | 1.5099(16) |

| | |
|---|---|
| C(12)-H(12A) | 0.9900 |
| C(12)-H(12B) | 0.9900 |
| C(13)-H(13A) | 0.9900 |
| C(13)-H(13B) | 0.9900 |
| C(14)-H(14A) | 0.9800 |
| C(14)-H(14B) | 0.9800 |
| C(14)-H(14C) | 0.9800 |
| C(15)-C(16) | 1.5366(15) |
| C(15)-H(15) | 1.0000 |
| C(16)-C(17) | 1.4135(16) |
| C(16)-C(21) | 1.4173(17) |
| C(17)-C(18) | 1.4007(17) |
| C(17)-C(22) | 1.5150(17) |
| C(18)-C(19) | 1.3844(18) |
| C(18)-H(18) | 0.9500 |
| C(19)-C(20) | 1.3919(18) |
| C(19)-C(23) | 1.5089(17) |
| C(20)-C(21) | 1.3952(17) |
| C(20)-H(20) | 0.9500 |
| C(21)-C(24) | 1.5146(16) |
| C(22)-H(22A) | 0.9800 |
| C(22)-H(22B) | 0.9800 |
| C(22)-H(22C) | 0.9800 |
| C(23)-H(23A) | 0.9800 |
| C(23)-H(23B) | 0.9800 |
| C(23)-H(23C) | 0.9800 |
| C(24)-H(24A) | 0.9800 |
| C(24)-H(24B) | 0.9800 |
| C(24)-H(24C) | 0.9800 |
| C(9)-N(1)-C(13) | 125.30(10) |
| C(9)-N(1)-C(7) | 119.43(10) |
| C(13)-N(1)-C(7) | 115.26(9) |
| C(15)-O(2)-H(2) | 103.5(12) |
| C(6)-C(1)-C(2) | 118.27(12) |
| C(6)-C(1)-C(7) | 119.01(11) |
| C(2)-C(1)-C(7) | 122.67(12) |
| C(3)-C(2)-C(1) | 120.47(13) |
| C(3)-C(2)-H(2A) | 119.8 |
| C(1)-C(2)-H(2A) | 119.8 |
| C(4)-C(3)-C(2) | 120.68(12) |
| C(4)-C(3)-H(3) | 119.7 |
| C(2)-C(3)-H(3) | 119.7 |
| C(3)-C(4)-C(5) | 119.43(12) |
| C(3)-C(4)-H(4) | 120.3 |
| C(5)-C(4)-H(4) | 120.3 |
| C(6)-C(5)-C(4) | 119.85(13) |

| | |
|---|---|
| C(6)-C(5)-H(5) | 120.1 |
| C(4)-C(5)-H(5) | 120.1 |
| C(5)-C(6)-C(1) | 121.28(12) |
| C(5)-C(6)-H(6) | 119.4 |
| C(1)-C(6)-H(6) | 119.4 |
| N(1)-C(7)-C(8) | 111.07(10) |
| N(1)-C(7)-C(1) | 109.08(9) |
| C(8)-C(7)-C(1) | 114.65(10) |
| N(1)-C(7)-H(7) | 107.2 |
| C(8)-C(7)-H(7) | 107.2 |
| C(1)-C(7)-H(7) | 107.2 |
| C(7)-C(8)-H(8A) | 109.5 |
| C(7)-C(8)-H(8B) | 109.5 |
| H(8A)-C(8)-H(8B) | 109.5 |
| C(7)-C(8)-H(8C) | 109.5 |
| H(8A)-C(8)-H(8C) | 109.5 |
| H(8B)-C(8)-H(8C) | 109.5 |
| O(1)-C(9)-N(1) | 121.23(10) |
| O(1)-C(9)-C(10) | 119.32(10) |
| N(1)-C(9)-C(10) | 119.22(10) |
| C(11)-C(10)-C(14) | 110.43(9) |
| C(11)-C(10)-C(9) | 112.69(9) |
| C(14)-C(10)-C(9) | 104.57(9) |
| C(11)-C(10)-C(15) | 111.64(9) |
| C(14)-C(10)-C(15) | 110.10(9) |
| C(9)-C(10)-C(15) | 107.14(9) |
| C(12)-C(11)-C(10) | 111.73(9) |
| C(12)-C(11)-H(11A) | 109.3 |
| C(10)-C(11)-H(11A) | 109.3 |
| C(12)-C(11)-H(11B) | 109.3 |
| C(10)-C(11)-H(11B) | 109.3 |
| H(11A)-C(11)-H(11B) | 107.9 |
| C(13)-C(12)-C(11) | 108.28(10) |
| C(13)-C(12)-H(12A) | 110.0 |
| C(11)-C(12)-H(12A) | 110.0 |
| C(13)-C(12)-H(12B) | 110.0 |
| C(11)-C(12)-H(12B) | 110.0 |
| H(12A)-C(12)-H(12B) | 108.4 |
| N(1)-C(13)-C(12) | 111.92(10) |
| N(1)-C(13)-H(13A) | 109.2 |
| C(12)-C(13)-H(13A) | 109.2 |
| N(1)-C(13)-H(13B) | 109.2 |
| C(12)-C(13)-H(13B) | 109.2 |
| H(13A)-C(13)-H(13B) | 107.9 |
| C(10)-C(14)-H(14A) | 109.5 |
| C(10)-C(14)-H(14B) | 109.5 |

| | |
|---|---|
| H(14A)-C(14)-H(14B) | 109.5 |
| C(10)-C(14)-H(14C) | 109.5 |
| H(14A)-C(14)-H(14C) | 109.5 |
| H(14B)-C(14)-H(14C) | 109.5 |
| O(2)-C(15)-C(16) | 113.76(9) |
| O(2)-C(15)-C(10) | 107.43(9) |
| C(16)-C(15)-C(10) | 114.60(9) |
| O(2)-C(15)-H(15) | 106.9 |
| C(16)-C(15)-H(15) | 106.9 |
| C(10)-C(15)-H(15) | 106.9 |
| C(17)-C(16)-C(21) | 117.87(10) |
| C(17)-C(16)-C(15) | 124.61(10) |
| C(21)-C(16)-C(15) | 117.51(10) |
| C(18)-C(17)-C(16) | 119.45(11) |
| C(18)-C(17)-C(22) | 114.82(10) |
| C(16)-C(17)-C(22) | 125.67(10) |
| C(19)-C(18)-C(17) | 122.94(11) |
| C(19)-C(18)-H(18) | 118.5 |
| C(17)-C(18)-H(18) | 118.5 |
| C(18)-C(19)-C(20) | 117.19(11) |
| C(18)-C(19)-C(23) | 120.92(11) |
| C(20)-C(19)-C(23) | 121.83(11) |
| C(19)-C(20)-C(21) | 122.10(11) |
| C(19)-C(20)-H(20) | 118.9 |
| C(21)-C(20)-H(20) | 118.9 |
| C(20)-C(21)-C(16) | 120.28(11) |
| C(20)-C(21)-C(24) | 117.02(11) |
| C(16)-C(21)-C(24) | 122.67(10) |
| C(17)-C(22)-H(22A) | 109.5 |
| C(17)-C(22)-H(22B) | 109.5 |
| H(22A)-C(22)-H(22B) | 109.5 |
| C(17)-C(22)-H(22C) | 109.5 |
| H(22A)-C(22)-H(22C) | 109.5 |
| H(22B)-C(22)-H(22C) | 109.5 |
| C(19)-C(23)-H(23A) | 109.5 |
| C(19)-C(23)-H(23B) | 109.5 |
| H(23A)-C(23)-H(23B) | 109.5 |
| C(19)-C(23)-H(23C) | 109.5 |
| H(23A)-C(23)-H(23C) | 109.5 |
| H(23B)-C(23)-H(23C) | 109.5 |
| C(21)-C(24)-H(24A) | 109.5 |
| C(21)-C(24)-H(24B) | 109.5 |
| H(24A)-C(24)-H(24B) | 109.5 |
| C(21)-C(24)-H(24C) | 109.5 |
| H(24A)-C(24)-H(24C) | 109.5 |
| H(24B)-C(24)-H(24C) | 109.5 |

Table C.4u Anisotropic displacement parameters (A^2 x 10^3) for nasymes. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| N(1) | 13(1) | 21(1) | 17(1) | -2(1) | 3(1) | 2(1) |
| O(1) | 13(1) | 25(1) | 20(1) | -2(1) | 4(1) | 4(1) |
| O(2) | 14(1) | 17(1) | 23(1) | -1(1) | 8(1) | -2(1) |
| C(1) | 12(1) | 27(1) | 19(1) | -1(1) | 2(1) | 4(1) |
| C(2) | 18(1) | 32(1) | 24(1) | -5(1) | 4(1) | 0(1) |
| C(3) | 20(1) | 43(1) | 20(1) | -5(1) | 6(1) | 6(1) |
| C(4) | 16(1) | 41(1) | 24(1) | 6(1) | 7(1) | 9(1) |
| C(5) | 22(1) | 28(1) | 30(1) | 5(1) | 9(1) | 4(1) |
| C(6) | 22(1) | 25(1) | 23(1) | -1(1) | 6(1) | 3(1) |
| C(7) | 14(1) | 25(1) | 19(1) | -4(1) | 2(1) | 0(1) |
| C(8) | 22(1) | 29(1) | 24(1) | -5(1) | 6(1) | -5(1) |
| C(9) | 13(1) | 18(1) | 17(1) | 1(1) | 5(1) | -1(1) |
| C(10) | 12(1) | 18(1) | 17(1) | -1(1) | 4(1) | 0(1) |
| C(11) | 12(1) | 22(1) | 18(1) | 0(1) | 4(1) | 2(1) |
| C(12) | 13(1) | 25(1) | 21(1) | 0(1) | 5(1) | 4(1) |
| C(13) | 17(1) | 21(1) | 22(1) | -2(1) | 5(1) | 4(1) |
| C(14) | 16(1) | 21(1) | 21(1) | 1(1) | 6(1) | -2(1) |
| C(15) | 12(1) | 16(1) | 18(1) | 0(1) | 4(1) | 0(1) |
| C(16) | 13(1) | 18(1) | 17(1) | 0(1) | 6(1) | -2(1) |
| C(17) | 13(1) | 19(1) | 19(1) | 1(1) | 7(1) | -1(1) |
| C(18) | 14(1) | 24(1) | 18(1) | 2(1) | 5(1) | 0(1) |
| C(19) | 18(1) | 23(1) | 19(1) | -1(1) | 6(1) | -4(1) |
| C(20) | 22(1) | 18(1) | 22(1) | -2(1) | 8(1) | -2(1) |
| C(21) | 16(1) | 19(1) | 19(1) | 1(1) | 7(1) | 0(1) |
| C(22) | 20(1) | 21(1) | 20(1) | 2(1) | 4(1) | 3(1) |
| C(23) | 27(1) | 28(1) | 23(1) | -2(1) | 1(1) | -6(1) |
| C(24) | 24(1) | 19(1) | 24(1) | -1(1) | 4(1) | 4(1) |

Table C.5u Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for nasymes.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 9252(18) | 5738(13) | 4047(15) | 39(5) |

| | | | | |
|---|---|---|---|---|
| H(2A) | 9336 | 6923 | 9997 | 30 |
| H(3) | 8655 | 6297 | 11414 | 33 |
| H(4) | 7705 | 4817 | 11278 | 32 |
| H(5) | 7429 | 3951 | 9701 | 32 |
| H(6) | 8165 | 4551 | 8305 | 28 |
| H(7) | 10065 | 5724 | 8058 | 23 |
| H(8A) | 10044 | 7343 | 7533 | 38 |
| H(8B) | 10531 | 7210 | 8785 | 38 |
| H(8C) | 9154 | 7579 | 8294 | 38 |
| H(11A) | 6756 | 6395 | 4875 | 21 |
| H(11B) | 5745 | 5567 | 4731 | 21 |
| H(12A) | 5474 | 6594 | 6081 | 23 |
| H(12B) | 5922 | 5581 | 6599 | 23 |
| H(13A) | 7457 | 7211 | 6625 | 24 |
| H(13B) | 7136 | 6735 | 7640 | 24 |
| H(14A) | 6613 | 4201 | 6261 | 28 |
| H(14B) | 7721 | 3679 | 5907 | 28 |
| H(14C) | 6444 | 3874 | 5059 | 28 |
| H(15) | 8807 | 4528 | 4668 | 18 |
| H(18) | 4933 | 5074 | 1413 | 22 |
| H(20) | 6631 | 2571 | 2187 | 24 |
| H(22A) | 6104 | 6479 | 2065 | 30 |
| H(22B) | 6931 | 6488 | 3255 | 30 |
| H(22C) | 5463 | 6364 | 3031 | 30 |
| H(23A) | 3928 | 3287 | 790 | 40 |
| H(23B) | 5049 | 2662 | 595 | 40 |
| H(23C) | 4782 | 3688 | 66 | 40 |
| H(24A) | 8183 | 2901 | 4569 | 34 |
| H(24B) | 9147 | 3291 | 3939 | 34 |
| H(24C) | 8321 | 2379 | 3514 | 34 |

Table C.6u Torsion angles [deg] for nasymes.

| | |
|---|---|
| C(6)-C(1)-C(2)-C(3) | 1.28(18) |
| C(7)-C(1)-C(2)-C(3) | -176.03(11) |
| C(1)-C(2)-C(3)-C(4) | -1.15(19) |
| C(2)-C(3)-C(4)-C(5) | -0.10(19) |
| C(3)-C(4)-C(5)-C(6) | 1.19(19) |
| C(4)-C(5)-C(6)-C(1) | -1.05(19) |
| C(2)-C(1)-C(6)-C(5) | -0.19(18) |
| C(7)-C(1)-C(6)-C(5) | 177.23(11) |
| C(9)-N(1)-C(7)-C(8) | 122.33(11) |
| C(13)-N(1)-C(7)-C(8) | -59.01(13) |
| C(9)-N(1)-C(7)-C(1) | -110.36(12) |

| | |
|---|---|
| C(13)-N(1)-C(7)-C(1) | 68.30(13) |
| C(6)-C(1)-C(7)-N(1) | 47.60(14) |
| C(2)-C(1)-C(7)-N(1) | -135.11(12) |
| C(6)-C(1)-C(7)-C(8) | 172.85(11) |
| C(2)-C(1)-C(7)-C(8) | -9.85(16) |
| C(13)-N(1)-C(9)-O(1) | 179.31(11) |
| C(7)-N(1)-C(9)-O(1) | -2.17(17) |
| C(13)-N(1)-C(9)-C(10) | -6.27(17) |
| C(7)-N(1)-C(9)-C(10) | 172.25(10) |
| O(1)-C(9)-C(10)-C(11) | -171.01(10) |
| N(1)-C(9)-C(10)-C(11) | 14.47(14) |
| O(1)-C(9)-C(10)-C(14) | 69.02(13) |
| N(1)-C(9)-C(10)-C(14) | -105.51(11) |
| O(1)-C(9)-C(10)-C(15) | -47.84(13) |
| N(1)-C(9)-C(10)-C(15) | 137.64(10) |
| C(14)-C(10)-C(11)-C(12) | 73.54(12) |
| C(9)-C(10)-C(11)-C(12) | -42.99(13) |
| C(15)-C(10)-C(11)-C(12) | -163.62(9) |
| C(10)-C(11)-C(12)-C(13) | 62.57(13) |
| C(9)-N(1)-C(13)-C(12) | 25.99(16) |
| C(7)-N(1)-C(13)-C(12) | -152.59(10) |
| C(11)-C(12)-C(13)-N(1) | -52.32(13) |
| C(11)-C(10)-C(15)-O(2) | 62.07(11) |
| C(14)-C(10)-C(15)-O(2) | -174.90(9) |
| C(9)-C(10)-C(15)-O(2) | -61.75(11) |
| C(11)-C(10)-C(15)-C(16) | -65.39(12) |
| C(14)-C(10)-C(15)-C(16) | 57.64(12) |
| C(9)-C(10)-C(15)-C(16) | 170.79(9) |
| O(2)-C(15)-C(16)-C(17) | -43.13(14) |
| C(10)-C(15)-C(16)-C(17) | 81.03(13) |
| O(2)-C(15)-C(16)-C(21) | 135.36(10) |
| C(10)-C(15)-C(16)-C(21) | -100.48(12) |
| C(21)-C(16)-C(17)-C(18) | 4.90(16) |
| C(15)-C(16)-C(17)-C(18) | -176.62(10) |
| C(21)-C(16)-C(17)-C(22) | -171.91(11) |
| C(15)-C(16)-C(17)-C(22) | 6.57(18) |
| C(16)-C(17)-C(18)-C(19) | -2.81(17) |
| C(22)-C(17)-C(18)-C(19) | 174.33(11) |
| C(17)-C(18)-C(19)-C(20) | -0.69(17) |
| C(17)-C(18)-C(19)-C(23) | -177.98(11) |
| C(18)-C(19)-C(20)-C(21) | 2.00(18) |
| C(23)-C(19)-C(20)-C(21) | 179.27(11) |
| C(19)-C(20)-C(21)-C(16) | 0.21(18) |
| C(19)-C(20)-C(21)-C(24) | -177.84(11) |
| C(17)-C(16)-C(21)-C(20) | -3.68(16) |
| C(15)-C(16)-C(21)-C(20) | 177.73(10) |

| | |
|---|---|
| C(17)-C(16)-C(21)-C(24) | 174.26(10) |
| C(15)-C(16)-C(21)-C(24) | -4.34(16) |

Table C.7u Hydrogen bonds for nasymes [A and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(2)-H(2)...O(1)#1 | 0.86(2) | 1.91(2) | 2.7576(12) | 168.2(18) |

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+1,-z+1

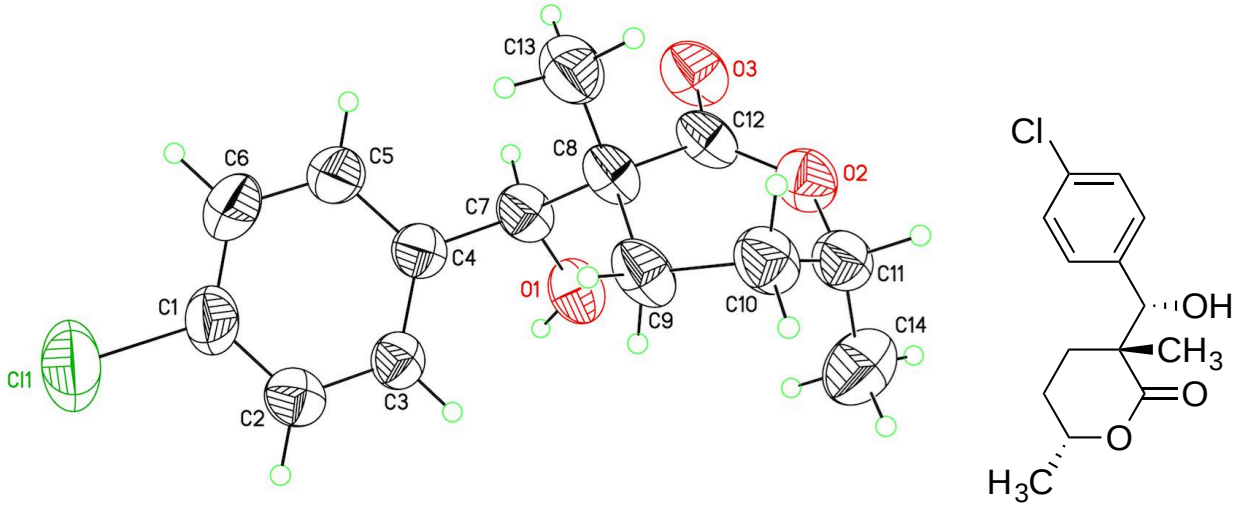



Figure C.22 Structure of ydbcl2m.

**Structure Determination.**

Colorless plates of **ydbcl2m** were grown from a dichloromethane/hexanes solution of the compound at 22 deg. C. A crystal of dimensions 0.17 x 0.15 x 0.04 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (ë = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 225(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ù. The exposure times were 1 sec. for the low angle images, 3 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 42048 reflections to a maximum 2è value of 138.78° of which 9778 were independent and 8489 were greater than 2ó(I). The final cell constants (Table 1) were based on the xyz centroids of 13071 reflections above 10ó(I). Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2016/6) software package, using the space group P1bar with Z = 8 for the formula $C_{14}H_{17}O_3Cl_2$. All non-hydrogen atoms

were refined anisotropically with the hydrogen atoms placed in a combination of idealized and refined positions. There are 4 crystallographically independent molecules in the asymmetric unit. Full matrix least-squares refinement based on $F^2$ converged at R1 = 0.0984 and wR2 = 0.2839 [based on I > 2sigma(I)], R1 = 0.1057 and wR2 = 0.2890 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.
G.M. Sheldrick (2015) "Crystal structure refinement with SHELXL", Acta Cryst., C71, 3-8 (Open Access). CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.
CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015).

Table C.1v Crystal data and structure refinement for ydbcl2m.

| | |
|---|---|
| Identification code | ydbcl2m |
| Empirical formula | C14 H17 Cl O3 |
| Formula weight | 268.72 |
| Temperature | 225(2) K |
| Wavelength | 1.54184 A |
| Crystal system, space group | Triclinic, P-1 |
| Unit cell dimensions | a = 9.1362(2) A alpha = 97.839(3) deg.<br>b = 9.1464(4) A beta = 96.475(2) deg.<br>c = 33.0302(11) A gamma = 90.136(2) deg. |
| Volume | 2716.44(16) A^3 |
| Z, Calculated density | 8, 1.314 Mg/m^3 |
| Absorption coefficient | 2.480 mm^-1 |
| F(000) | 1136 |
| Crystal size | 0.170 x 0.150 x 0.040 mm |
| Theta range for data collection | 2.719 to 69.393 deg. |
| Limiting indices | -11<=h<=11, -8<=k<=10, -40<=l<=39 |
| Reflections collected / unique | 42028 / 9778 [R(int) = 0.0436] |
| Completeness to theta = 67.684 | 97.6 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00000 and 0.84174 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 9778 / 6 / 674 |
| Goodness-of-fit on F^2 | 1.096 |
| Final R indices [I>2sigma(I)] | R1 = 0.0984, wR2 = 0.2839 |
| R indices (all data) | R1 = 0.1057, wR2 = 0.2890 |
| Extinction coefficient | 0.0029(3) |
| Largest diff. peak and hole | 0.644 and -0.348 e.A^-3 |

Table C.2v Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x10^3) for ydbcl2m. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Cl(1) | 8959(3) | 7609(2) | 2730(1) | 103(1) |
| Cl(2) | 2254(2) | 5972(2) | 2285(1) | 92(1) |
| Cl(3) | -2806(2) | 918(2) | 2252(1) | 90(1) |
| Cl(4) | 3953(2) | 12651(2) | 2752(1) | 90(1) |
| O(1) | 8063(4) | 3477(4) | 4221(1) | 59(1) |
| O(2) | 10403(4) | 960(4) | 4569(1) | 60(1) |
| O(3) | 8731(4) | 47(4) | 4075(1) | 68(1) |
| O(4) | 6454(4) | 3756(4) | 777(1) | 54(1) |
| O(5) | 9015(4) | 5782(4) | 432(1) | 57(1) |
| O(6) | 9900(4) | 4548(4) | 921(1) | 65(1) |
| O(7) | 1499(4) | 1977(4) | 787(1) | 57(1) |
| O(8) | 4022(4) | -388(4) | 433(1) | 61(1) |
| O(9) | 4905(4) | 1293(4) | 926(1) | 67(1) |
| O(10) | 6280(4) | 8420(4) | 4200(1) | 56(1) |
| O(11) | 4217(4) | 5944(4) | 4566(1) | 60(1) |
| O(12) | 5458(4) | 5019(4) | 4069(1) | 62(1) |
| C(1) | 8834(7) | 6272(7) | 3055(2) | 63(2) |
| C(2) | 8969(5) | 6674(6) | 3469(2) | 51(1) |
| C(3) | 8856(5) | 5605(6) | 3723(2) | 47(1) |
| C(4) | 8613(5) | 4134(5) | 3563(2) | 47(1) |
| C(5) | 8455(8) | 3760(7) | 3137(2) | 76(2) |
| C(6) | 8590(10) | 4818(8) | 2883(2) | 88(2) |
| C(7) | 8517(5) | 2944(6) | 3833(2) | 52(1) |
| C(8) | 10007(5) | 2172(5) | 3934(2) | 47(1) |
| C(9) | 11177(5) | 3318(6) | 4162(2) | 58(1) |
| C(10) | 12340(6) | 2608(7) | 4426(2) | 61(1) |
| C(11) | 11644(6) | 1949(6) | 4745(2) | 56(1) |
| C(12) | 9660(5) | 1001(5) | 4200(2) | 51(1) |
| C(13) | 10537(7) | 1360(7) | 3548(2) | 66(2) |
| C(14) | 11155(8) | 2964(9) | 5094(2) | 85(2) |
| C(15) | 3607(6) | 5533(6) | 1958(2) | 57(1) |
| C(16) | 3231(6) | 5359(5) | 1543(2) | 50(1) |
| C(17) | 4309(5) | 5021(5) | 1283(2) | 44(1) |
| C(18) | 5770(5) | 4867(5) | 1442(2) | 45(1) |
| C(19) | 6089(6) | 5031(8) | 1866(2) | 67(2) |
| C(20) | 5042(7) | 5343(8) | 2122(2) | 73(2) |
| C(21) | 6967(5) | 4537(5) | 1168(2) | 46(1) |
| C(22) | 7755(5) | 5943(5) | 1069(2) | 48(1) |
| C(23) | 6643(6) | 6938(6) | 847(2) | 61(2) |
| C(24) | 7353(7) | 7840(7) | 577(2) | 64(1) |
| C(25) | 8029(6) | 6857(6) | 259(2) | 58(1) |
| C(26) | 8940(5) | 5375(5) | 801(2) | 46(1) |

| | | | | |
|---|---|---|---|---|
| C(27) | 8560(7) | 6807(7) | 1463(2) | 69(2) |
| C(28) | 7031(9) | 6068(8) | -90(2) | 82(2) |
| C(29) | -1419(6) | 1162(7) | 1938(2) | 61(1) |
| C(30) | -1771(6) | 1030(6) | 1523(2) | 50(1) |
| C(31) | -679(5) | 1180(5) | 1277(2) | 46(1) |
| C(32) | 778(5) | 1437(5) | 1445(2) | 48(1) |
| C(33) | 1077(6) | 1616(8) | 1864(2) | 72(2) |
| C(34) | 7(7) | 1464(9) | 2115(2) | 81(2) |
| C(35) | 1996(5) | 1539(5) | 1175(2) | 51(1) |
| C(36) | 2767(5) | 43(5) | 1067(2) | 49(1) |
| C(37) | 1631(6) | -1147(6) | 840(2) | 59(1) |
| C(38) | 2351(6) | -2322(6) | 564(2) | 60(1) |
| C(39) | 3024(6) | -1629(6) | 246(2) | 58(1) |
| C(40) | 3956(5) | 362(6) | 803(2) | 51(1) |
| C(41) | 3545(7) | -484(8) | 1453(2) | 70(2) |
| C(42) | 2032(8) | -1123(8) | -88(2) | 80(2) |
| C(43) | 4437(6) | 11273(6) | 3061(2) | 54(1) |
| C(44) | 4705(5) | 11657(6) | 3477(2) | 49(1) |
| C(45) | 5049(5) | 10564(5) | 3718(2) | 45(1) |
| C(46) | 5135(5) | 9104(5) | 3551(2) | 46(1) |
| C(47) | 4896(7) | 8767(7) | 3123(2) | 65(2) |
| C(48) | 4521(9) | 9854(8) | 2877(2) | 76(2) |
| C(49) | 5463(5) | 7898(6) | 3813(2) | 48(1) |
| C(50) | 4072(5) | 7132(5) | 3924(2) | 48(1) |
| C(51) | 3098(5) | 8296(6) | 4155(2) | 58(1) |
| C(52) | 2181(6) | 7619(6) | 4433(2) | 60(1) |
| C(53) | 3154(6) | 6957(6) | 4747(2) | 56(1) |
| C(54) | 4631(5) | 5977(5) | 4195(2) | 48(1) |
| C(55) | 3943(8) | 7964(9) | 5090(2) | 82(2) |
| C(56) | 3213(7) | 6320(7) | 3539(2) | 68(2) |

Table C.3v Bond lengths [A] and angles [deg] for ydbcl2m.

| | |
|---|---|
| Cl(1)-C(1) | 1.746(6) |
| Cl(2)-C(15) | 1.744(6) |
| Cl(3)-C(29) | 1.756(6) |
| Cl(4)-C(43) | 1.753(5) |
| O(1)-C(7) | 1.415(7) |
| O(1)-H(1) | 0.94(4) |
| O(2)-C(12) | 1.331(7) |
| O(2)-C(11) | 1.465(6) |
| O(3)-C(12) | 1.213(6) |
| O(4)-C(21) | 1.416(6) |
| O(4)-H(4) | 0.94(4) |

| | |
|---|---|
| O(5)-C(26) | 1.330(6) |
| O(5)-C(25) | 1.465(6) |
| O(6)-C(26) | 1.226(6) |
| O(7)-C(35) | 1.421(7) |
| O(7)-H(7) | 0.93(4) |
| O(8)-C(40) | 1.325(7) |
| O(8)-C(39) | 1.476(7) |
| O(9)-C(40) | 1.211(6) |
| O(10)-C(49) | 1.427(6) |
| O(10)-H(10) | 0.94(4) |
| O(11)-C(54) | 1.326(7) |
| O(11)-C(53) | 1.465(7) |
| O(12)-C(54) | 1.219(6) |
| C(1)-C(2) | 1.359(8) |
| C(1)-C(6) | 1.380(10) |
| C(2)-C(3) | 1.383(7) |
| C(2)-H(2) | 0.9400 |
| C(3)-C(4) | 1.385(7) |
| C(3)-H(3) | 0.9400 |
| C(4)-C(5) | 1.392(8) |
| C(4)-C(7) | 1.506(7) |
| C(5)-C(6) | 1.379(10) |
| C(5)-H(5) | 0.9400 |
| C(6)-H(6) | 0.9400 |
| C(7)-C(8) | 1.559(6) |
| C(7)-H(7A) | 0.9900 |
| C(8)-C(13) | 1.515(8) |
| C(8)-C(12) | 1.529(7) |
| C(8)-C(9) | 1.552(7) |
| C(9)-C(10) | 1.504(7) |
| C(9)-H(9A) | 0.9800 |
| C(9)-H(9B) | 0.9800 |
| C(10)-C(11) | 1.483(8) |
| C(10)-H(10A) | 0.9800 |
| C(10)-H(10B) | 0.9800 |
| C(11)-C(14) | 1.488(9) |
| C(11)-H(11) | 0.9900 |
| C(13)-H(13A) | 0.9700 |
| C(13)-H(13B) | 0.9700 |
| C(13)-H(13C) | 0.9700 |
| C(14)-H(14A) | 0.9700 |
| C(14)-H(14B) | 0.9700 |
| C(14)-H(14C) | 0.9700 |
| C(15)-C(16) | 1.363(8) |
| C(15)-C(20) | 1.382(9) |
| C(16)-C(17) | 1.387(7) |

| | |
|---|---|
| C(16)-H(16) | 0.9400 |
| C(17)-C(18) | 1.393(6) |
| C(17)-H(17) | 0.9400 |
| C(18)-C(19) | 1.384(7) |
| C(18)-C(21) | 1.502(7) |
| C(19)-C(20) | 1.354(9) |
| C(19)-H(19) | 0.9400 |
| C(20)-H(20) | 0.9400 |
| C(21)-C(22) | 1.564(7) |
| C(21)-H(21) | 0.9900 |
| C(22)-C(26) | 1.522(7) |
| C(22)-C(27) | 1.537(8) |
| C(22)-C(23) | 1.553(7) |
| C(23)-C(24) | 1.493(8) |
| C(23)-H(23A) | 0.9800 |
| C(23)-H(23B) | 0.9800 |
| C(24)-C(25) | 1.478(8) |
| C(24)-H(24A) | 0.9800 |
| C(24)-H(24B) | 0.9800 |
| C(25)-C(28) | 1.487(8) |
| C(25)-H(25) | 0.9900 |
| C(27)-H(27A) | 0.9700 |
| C(27)-H(27B) | 0.9700 |
| C(27)-H(27C) | 0.9700 |
| C(28)-H(28A) | 0.9700 |
| C(28)-H(28B) | 0.9700 |
| C(28)-H(28C) | 0.9700 |
| C(29)-C(30) | 1.362(8) |
| C(29)-C(34) | 1.378(9) |
| C(30)-C(31) | 1.373(7) |
| C(30)-H(30) | 0.9400 |
| C(31)-C(32) | 1.390(7) |
| C(31)-H(31) | 0.9400 |
| C(32)-C(33) | 1.369(8) |
| C(32)-C(35) | 1.511(7) |
| C(33)-C(34) | 1.370(9) |
| C(33)-H(33) | 0.9400 |
| C(34)-H(34) | 0.9400 |
| C(35)-C(36) | 1.557(7) |
| C(35)-H(35) | 0.9900 |
| C(36)-C(40) | 1.519(7) |
| C(36)-C(41) | 1.524(8) |
| C(36)-C(37) | 1.556(7) |
| C(37)-C(38) | 1.515(7) |
| C(37)-H(37A) | 0.9800 |
| C(37)-H(37B) | 0.9800 |

| | |
|---|---|
| C(38)-C(39) | 1.484(8) |
| C(38)-H(38A) | 0.9800 |
| C(38)-H(38B) | 0.9800 |
| C(39)-C(42) | 1.473(8) |
| C(39)-H(39) | 0.9900 |
| C(41)-H(41A) | 0.9700 |
| C(41)-H(41B) | 0.9700 |
| C(41)-H(41C) | 0.9700 |
| C(42)-H(42A) | 0.9700 |
| C(42)-H(42B) | 0.9700 |
| C(42)-H(42C) | 0.9700 |
| C(43)-C(48) | 1.361(9) |
| C(43)-C(44) | 1.368(7) |
| C(44)-C(45) | 1.376(7) |
| C(44)-H(44) | 0.9400 |
| C(45)-C(46) | 1.380(7) |
| C(45)-H(45) | 0.9400 |
| C(46)-C(47) | 1.399(7) |
| C(46)-C(49) | 1.503(7) |
| C(47)-C(48) | 1.387(9) |
| C(47)-H(47) | 0.9400 |
| C(48)-H(48) | 0.9400 |
| C(49)-C(50) | 1.553(6) |
| C(49)-H(49) | 0.9900 |
| C(50)-C(56) | 1.518(8) |
| C(50)-C(54) | 1.527(7) |
| C(50)-C(51) | 1.563(7) |
| C(51)-C(52) | 1.500(8) |
| C(51)-H(51A) | 0.9800 |
| C(51)-H(51B) | 0.9800 |
| C(52)-C(53) | 1.484(8) |
| C(52)-H(52A) | 0.9800 |
| C(52)-H(52B) | 0.9800 |
| C(53)-C(55) | 1.476(9) |
| C(53)-H(53) | 0.9900 |
| C(55)-H(55A) | 0.9700 |
| C(55)-H(55B) | 0.9700 |
| C(55)-H(55C) | 0.9700 |
| C(56)-H(56A) | 0.9700 |
| C(56)-H(56B) | 0.9700 |
| C(56)-H(56C) | 0.9700 |
| C(7)-O(1)-H(1) | 121(5) |
| C(12)-O(2)-C(11) | 124.2(4) |
| C(21)-O(4)-H(4) | 112(5) |
| C(26)-O(5)-C(25) | 123.5(4) |
| C(35)-O(7)-H(7) | 112(6) |

| | |
|---|---|
| C(40)-O(8)-C(39) | 124.4(4) |
| C(49)-O(10)-H(10) | 104(3) |
| C(54)-O(11)-C(53) | 123.9(4) |
| C(2)-C(1)-C(6) | 121.3(6) |
| C(2)-C(1)-Cl(1) | 119.9(5) |
| C(6)-C(1)-Cl(1) | 118.8(5) |
| C(1)-C(2)-C(3) | 119.3(5) |
| C(1)-C(2)-H(2) | 120.3 |
| C(3)-C(2)-H(2) | 120.3 |
| C(2)-C(3)-C(4) | 121.2(5) |
| C(2)-C(3)-H(3) | 119.4 |
| C(4)-C(3)-H(3) | 119.4 |
| C(3)-C(4)-C(5) | 118.2(5) |
| C(3)-C(4)-C(7) | 122.2(5) |
| C(5)-C(4)-C(7) | 119.6(5) |
| C(6)-C(5)-C(4) | 120.9(6) |
| C(6)-C(5)-H(5) | 119.6 |
| C(4)-C(5)-H(5) | 119.6 |
| C(1)-C(6)-C(5) | 119.1(6) |
| C(1)-C(6)-H(6) | 120.4 |
| C(5)-C(6)-H(6) | 120.4 |
| O(1)-C(7)-C(4) | 113.0(4) |
| O(1)-C(7)-C(8) | 104.8(4) |
| C(4)-C(7)-C(8) | 113.9(4) |
| O(1)-C(7)-H(7A) | 108.3 |
| C(4)-C(7)-H(7A) | 108.3 |
| C(8)-C(7)-H(7A) | 108.3 |
| C(13)-C(8)-C(12) | 106.8(4) |
| C(13)-C(8)-C(9) | 111.2(5) |
| C(12)-C(8)-C(9) | 112.0(4) |
| C(13)-C(8)-C(7) | 111.1(4) |
| C(12)-C(8)-C(7) | 105.4(4) |
| C(9)-C(8)-C(7) | 110.2(4) |
| C(10)-C(9)-C(8) | 111.6(4) |
| C(10)-C(9)-H(9A) | 109.3 |
| C(8)-C(9)-H(9A) | 109.3 |
| C(10)-C(9)-H(9B) | 109.3 |
| C(8)-C(9)-H(9B) | 109.3 |
| H(9A)-C(9)-H(9B) | 108.0 |
| C(11)-C(10)-C(9) | 109.3(5) |
| C(11)-C(10)-H(10A) | 109.8 |
| C(9)-C(10)-H(10A) | 109.8 |
| C(11)-C(10)-H(10B) | 109.8 |
| C(9)-C(10)-H(10B) | 109.8 |
| H(10A)-C(10)-H(10B) | 108.3 |
| O(2)-C(11)-C(10) | 112.3(5) |

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|---|---|
| O(2)-C(11)-C(14) | 107.9(5) |
| C(10)-C(11)-C(14) | 118.0(6) |
| O(2)-C(11)-H(11) | 105.9 |
| C(10)-C(11)-H(11) | 105.9 |
| C(14)-C(11)-H(11) | 105.9 |
| O(3)-C(12)-O(2) | 117.8(5) |
| O(3)-C(12)-C(8) | 120.8(5) |
| O(2)-C(12)-C(8) | 121.3(4) |
| C(8)-C(13)-H(13A) | 109.5 |
| C(8)-C(13)-H(13B) | 109.5 |
| H(13A)-C(13)-H(13B) | 109.5 |
| C(8)-C(13)-H(13C) | 109.5 |
| H(13A)-C(13)-H(13C) | 109.5 |
| H(13B)-C(13)-H(13C) | 109.5 |
| C(11)-C(14)-H(14A) | 109.5 |
| C(11)-C(14)-H(14B) | 109.5 |
| H(14A)-C(14)-H(14B) | 109.5 |
| C(11)-C(14)-H(14C) | 109.5 |
| H(14A)-C(14)-H(14C) | 109.5 |
| H(14B)-C(14)-H(14C) | 109.5 |
| C(16)-C(15)-C(20) | 120.7(5) |
| C(16)-C(15)-Cl(2) | 119.6(4) |
| C(20)-C(15)-Cl(2) | 119.7(4) |
| C(15)-C(16)-C(17) | 119.6(5) |
| C(15)-C(16)-H(16) | 120.2 |
| C(17)-C(16)-H(16) | 120.2 |
| C(16)-C(17)-C(18) | 120.6(5) |
| C(16)-C(17)-H(17) | 119.7 |
| C(18)-C(17)-H(17) | 119.7 |
| C(19)-C(18)-C(17) | 117.5(5) |
| C(19)-C(18)-C(21) | 120.7(4) |
| C(17)-C(18)-C(21) | 121.8(4) |
| C(20)-C(19)-C(18) | 122.3(5) |
| C(20)-C(19)-H(19) | 118.8 |
| C(18)-C(19)-H(19) | 118.8 |
| C(19)-C(20)-C(15) | 119.2(5) |
| C(19)-C(20)-H(20) | 120.4 |
| C(15)-C(20)-H(20) | 120.4 |
| O(4)-C(21)-C(18) | 113.4(4) |
| O(4)-C(21)-C(22) | 104.3(4) |
| C(18)-C(21)-C(22) | 113.9(4) |
| O(4)-C(21)-H(21) | 108.3 |
| C(18)-C(21)-H(21) | 108.3 |
| C(22)-C(21)-H(21) | 108.3 |
| C(26)-C(22)-C(27) | 106.5(4) |
| C(26)-C(22)-C(23) | 112.0(4) |

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|---|---|
| C(27)-C(22)-C(23) | 110.9(5) |
| C(26)-C(22)-C(21) | 105.6(4) |
| C(27)-C(22)-C(21) | 110.5(5) |
| C(23)-C(22)-C(21) | 111.0(4) |
| C(24)-C(23)-C(22) | 112.6(4) |
| C(24)-C(23)-H(23A) | 109.1 |
| C(22)-C(23)-H(23A) | 109.1 |
| C(24)-C(23)-H(23B) | 109.1 |
| C(22)-C(23)-H(23B) | 109.1 |
| H(23A)-C(23)-H(23B) | 107.8 |
| C(25)-C(24)-C(23) | 109.7(5) |
| C(25)-C(24)-H(24A) | 109.7 |
| C(23)-C(24)-H(24A) | 109.7 |
| C(25)-C(24)-H(24B) | 109.7 |
| C(23)-C(24)-H(24B) | 109.7 |
| H(24A)-C(24)-H(24B) | 108.2 |
| O(5)-C(25)-C(24) | 112.8(5) |
| O(5)-C(25)-C(28) | 108.6(5) |
| C(24)-C(25)-C(28) | 117.7(5) |
| O(5)-C(25)-H(25) | 105.6 |
| C(24)-C(25)-H(25) | 105.6 |
| C(28)-C(25)-H(25) | 105.6 |
| O(6)-C(26)-O(5) | 116.7(4) |
| O(6)-C(26)-C(22) | 121.4(5) |
| O(5)-C(26)-C(22) | 121.9(4) |
| C(22)-C(27)-H(27A) | 109.5 |
| C(22)-C(27)-H(27B) | 109.5 |
| H(27A)-C(27)-H(27B) | 109.5 |
| C(22)-C(27)-H(27C) | 109.5 |
| H(27A)-C(27)-H(27C) | 109.5 |
| H(27B)-C(27)-H(27C) | 109.5 |
| C(25)-C(28)-H(28A) | 109.5 |
| C(25)-C(28)-H(28B) | 109.5 |
| H(28A)-C(28)-H(28B) | 109.5 |
| C(25)-C(28)-H(28C) | 109.5 |
| H(28A)-C(28)-H(28C) | 109.5 |
| H(28B)-C(28)-H(28C) | 109.5 |
| C(30)-C(29)-C(34) | 121.1(6) |
| C(30)-C(29)-Cl(3) | 119.3(4) |
| C(34)-C(29)-Cl(3) | 119.6(5) |
| C(29)-C(30)-C(31) | 119.3(5) |
| C(29)-C(30)-H(30) | 120.4 |
| C(31)-C(30)-H(30) | 120.4 |
| C(30)-C(31)-C(32) | 121.0(5) |
| C(30)-C(31)-H(31) | 119.5 |
| C(32)-C(31)-H(31) | 119.5 |

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| C(33)-C(32)-C(31) | 117.8(5) |
| C(33)-C(32)-C(35) | 120.8(5) |
| C(31)-C(32)-C(35) | 121.4(5) |
| C(32)-C(33)-C(34) | 122.1(5) |
| C(32)-C(33)-H(33) | 119.0 |
| C(34)-C(33)-H(33) | 119.0 |
| C(33)-C(34)-C(29) | 118.6(6) |
| C(33)-C(34)-H(34) | 120.7 |
| C(29)-C(34)-H(34) | 120.7 |
| O(7)-C(35)-C(32) | 113.4(4) |
| O(7)-C(35)-C(36) | 104.4(4) |
| C(32)-C(35)-C(36) | 113.3(4) |
| O(7)-C(35)-H(35) | 108.5 |
| C(32)-C(35)-H(35) | 108.5 |
| C(36)-C(35)-H(35) | 108.5 |
| C(40)-C(36)-C(41) | 106.9(4) |
| C(40)-C(36)-C(37) | 112.3(5) |
| C(41)-C(36)-C(37) | 110.2(5) |
| C(40)-C(36)-C(35) | 105.8(4) |
| C(41)-C(36)-C(35) | 111.0(5) |
| C(37)-C(36)-C(35) | 110.5(4) |
| C(38)-C(37)-C(36) | 111.8(4) |
| C(38)-C(37)-H(37A) | 109.3 |
| C(36)-C(37)-H(37A) | 109.3 |
| C(38)-C(37)-H(37B) | 109.3 |
| C(36)-C(37)-H(37B) | 109.3 |
| H(37A)-C(37)-H(37B) | 107.9 |
| C(39)-C(38)-C(37) | 109.4(5) |
| C(39)-C(38)-H(38A) | 109.8 |
| C(37)-C(38)-H(38A) | 109.8 |
| C(39)-C(38)-H(38B) | 109.8 |
| C(37)-C(38)-H(38B) | 109.8 |
| H(38A)-C(38)-H(38B) | 108.2 |
| C(42)-C(39)-O(8) | 108.0(5) |
| C(42)-C(39)-C(38) | 117.9(5) |
| O(8)-C(39)-C(38) | 111.6(5) |
| C(42)-C(39)-H(39) | 106.2 |
| O(8)-C(39)-H(39) | 106.2 |
| C(38)-C(39)-H(39) | 106.2 |
| O(9)-C(40)-O(8) | 117.0(5) |
| O(9)-C(40)-C(36) | 121.3(5) |
| O(8)-C(40)-C(36) | 121.7(4) |
| C(36)-C(41)-H(41A) | 109.5 |
| C(36)-C(41)-H(41B) | 109.5 |
| H(41A)-C(41)-H(41B) | 109.5 |
| C(36)-C(41)-H(41C) | 109.5 |

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|---|---|
| H(41A)-C(41)-H(41C) | 109.5 |
| H(41B)-C(41)-H(41C) | 109.5 |
| C(39)-C(42)-H(42A) | 109.5 |
| C(39)-C(42)-H(42B) | 109.5 |
| H(42A)-C(42)-H(42B) | 109.5 |
| C(39)-C(42)-H(42C) | 109.5 |
| H(42A)-C(42)-H(42C) | 109.5 |
| H(42B)-C(42)-H(42C) | 109.5 |
| C(48)-C(43)-C(44) | 122.2(5) |
| C(48)-C(43)-Cl(4) | 118.9(4) |
| C(44)-C(43)-Cl(4) | 118.9(4) |
| C(43)-C(44)-C(45) | 118.6(5) |
| C(43)-C(44)-H(44) | 120.7 |
| C(45)-C(44)-H(44) | 120.7 |
| C(44)-C(45)-C(46) | 121.9(5) |
| C(44)-C(45)-H(45) | 119.0 |
| C(46)-C(45)-H(45) | 119.0 |
| C(45)-C(46)-C(47) | 117.5(5) |
| C(45)-C(46)-C(49) | 122.3(4) |
| C(47)-C(46)-C(49) | 120.2(5) |
| C(48)-C(47)-C(46) | 121.0(5) |
| C(48)-C(47)-H(47) | 119.5 |
| C(46)-C(47)-H(47) | 119.5 |
| C(43)-C(48)-C(47) | 118.7(5) |
| C(43)-C(48)-H(48) | 120.7 |
| C(47)-C(48)-H(48) | 120.7 |
| O(10)-C(49)-C(46) | 112.6(4) |
| O(10)-C(49)-C(50) | 104.7(4) |
| C(46)-C(49)-C(50) | 114.1(4) |
| O(10)-C(49)-H(49) | 108.4 |
| C(46)-C(49)-H(49) | 108.4 |
| C(50)-C(49)-H(49) | 108.4 |
| C(56)-C(50)-C(54) | 107.5(4) |
| C(56)-C(50)-C(49) | 110.2(5) |
| C(54)-C(50)-C(49) | 106.1(4) |
| C(56)-C(50)-C(51) | 111.3(4) |
| C(54)-C(50)-C(51) | 111.5(4) |
| C(49)-C(50)-C(51) | 110.1(4) |
| C(52)-C(51)-C(50) | 112.1(4) |
| C(52)-C(51)-H(51A) | 109.2 |
| C(50)-C(51)-H(51A) | 109.2 |
| C(52)-C(51)-H(51B) | 109.2 |
| C(50)-C(51)-H(51B) | 109.2 |
| H(51A)-C(51)-H(51B) | 107.9 |
| C(53)-C(52)-C(51) | 109.7(5) |
| C(53)-C(52)-H(52A) | 109.7 |

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|---|---|
| C(51)-C(52)-H(52A) | 109.7 |
| C(53)-C(52)-H(52B) | 109.7 |
| C(51)-C(52)-H(52B) | 109.7 |
| H(52A)-C(52)-H(52B) | 108.2 |
| O(11)-C(53)-C(55) | 108.6(5) |
| O(11)-C(53)-C(52) | 112.5(5) |
| C(55)-C(53)-C(52) | 117.9(5) |
| O(11)-C(53)-H(53) | 105.6 |
| C(55)-C(53)-H(53) | 105.6 |
| C(52)-C(53)-H(53) | 105.6 |
| O(12)-C(54)-O(11) | 117.5(5) |
| O(12)-C(54)-C(50) | 120.3(5) |
| O(11)-C(54)-C(50) | 122.2(4) |
| C(53)-C(55)-H(55A) | 109.5 |
| C(53)-C(55)-H(55B) | 109.5 |
| H(55A)-C(55)-H(55B) | 109.5 |
| C(53)-C(55)-H(55C) | 109.5 |
| H(55A)-C(55)-H(55C) | 109.5 |
| H(55B)-C(55)-H(55C) | 109.5 |
| C(50)-C(56)-H(56A) | 109.5 |
| C(50)-C(56)-H(56B) | 109.5 |
| H(56A)-C(56)-H(56B) | 109.5 |
| C(50)-C(56)-H(56C) | 109.5 |
| H(56A)-C(56)-H(56C) | 109.5 |
| H(56B)-C(56)-H(56C) | 109.5 |

Table C.4v Anisotropic displacement parameters (A^2 x 10^3) for ydbcl2m. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Cl(1) | 149(2) | 98(1) | 73(1) | 42(1) | 24(1) | 30(1) |
| Cl(2) | 78(1) | 122(2) | 74(1) | -6(1) | 32(1) | 2(1) |
| Cl(3) | 79(1) | 125(2) | 63(1) | -4(1) | 25(1) | -14(1) |
| Cl(4) | 120(2) | 82(1) | 68(1) | 32(1) | -22(1) | -11(1) |
| O(1) | 42(2) | 64(2) | 74(2) | 20(2) | 11(2) | 12(2) |
| O(2) | 64(2) | 52(2) | 68(2) | 17(2) | 9(2) | -9(2) |
| O(3) | 53(2) | 52(2) | 99(3) | 15(2) | 2(2) | -17(2) |
| O(4) | 60(2) | 46(2) | 58(2) | 3(2) | 14(2) | -9(2) |
| O(5) | 48(2) | 61(2) | 64(2) | 7(2) | 10(2) | 12(2) |
| O(6) | 49(2) | 62(2) | 87(3) | 17(2) | 13(2) | 18(2) |
| O(7) | 57(2) | 46(2) | 71(2) | 13(2) | 13(2) | 13(2) |
| O(8) | 50(2) | 65(2) | 70(2) | 11(2) | 12(2) | -10(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O(9) | 48(2) | 59(2) | 96(3) | 12(2) | 9(2) | -14(2) |
| O(10) | 40(2) | 59(2) | 70(2) | 21(2) | -1(2) | -10(2) |
| O(11) | 65(2) | 51(2) | 65(2) | 15(2) | 2(2) | 14(2) |
| O(12) | 52(2) | 47(2) | 89(3) | 13(2) | 10(2) | 14(2) |
| C(1) | 74(4) | 65(4) | 52(3) | 19(3) | 3(3) | 18(3) |
| C(2) | 41(2) | 50(3) | 60(3) | 6(2) | 4(2) | 7(2) |
| C(3) | 40(2) | 52(3) | 49(3) | 8(2) | 2(2) | 6(2) |
| C(4) | 36(2) | 47(3) | 56(3) | 5(2) | -7(2) | 4(2) |
| C(5) | 102(5) | 55(4) | 59(3) | -1(3) | -31(3) | 14(3) |
| C(6) | 130(7) | 80(5) | 45(3) | 5(3) | -15(4) | 23(4) |
| C(7) | 37(2) | 49(3) | 69(3) | 11(2) | -1(2) | 1(2) |
| C(8) | 33(2) | 40(3) | 70(3) | 16(2) | 4(2) | -1(2) |
| C(9) | 39(3) | 43(3) | 92(4) | 23(3) | -1(2) | -8(2) |
| C(10) | 48(3) | 55(3) | 79(4) | 11(3) | -2(3) | 3(2) |
| C(11) | 52(3) | 48(3) | 66(3) | 9(2) | 1(2) | 0(2) |
| C(12) | 37(2) | 38(3) | 80(4) | 13(2) | 11(2) | 1(2) |
| C(13) | 68(4) | 61(4) | 73(4) | 17(3) | 13(3) | 15(3) |
| C(14) | 75(4) | 110(6) | 67(4) | 0(4) | 7(3) | 3(4) |
| C(15) | 57(3) | 60(3) | 56(3) | 7(2) | 13(2) | 2(2) |
| C(16) | 47(3) | 44(3) | 60(3) | 9(2) | 5(2) | 0(2) |
| C(17) | 43(2) | 43(3) | 48(3) | 12(2) | 2(2) | 1(2) |
| C(18) | 42(2) | 44(3) | 49(3) | 13(2) | 0(2) | 1(2) |
| C(19) | 50(3) | 99(5) | 53(3) | 17(3) | 0(2) | 5(3) |
| C(20) | 68(4) | 103(5) | 48(3) | 9(3) | 5(3) | -2(3) |
| C(21) | 48(3) | 38(3) | 54(3) | 9(2) | 9(2) | 5(2) |
| C(22) | 42(2) | 38(3) | 65(3) | 5(2) | 12(2) | 4(2) |
| C(23) | 44(3) | 40(3) | 106(5) | 20(3) | 22(3) | 11(2) |
| C(24) | 56(3) | 57(3) | 79(4) | 14(3) | 8(3) | 4(3) |
| C(25) | 54(3) | 55(3) | 63(3) | 11(2) | -2(2) | 3(2) |
| C(26) | 34(2) | 37(2) | 66(3) | 2(2) | 6(2) | 6(2) |
| C(27) | 54(3) | 70(4) | 79(4) | -9(3) | 9(3) | -12(3) |
| C(28) | 91(5) | 84(5) | 66(4) | 7(3) | -8(3) | -1(4) |
| C(29) | 55(3) | 66(4) | 60(3) | -3(3) | 10(2) | 1(3) |
| C(30) | 48(3) | 45(3) | 54(3) | -1(2) | 0(2) | 0(2) |
| C(31) | 42(2) | 43(3) | 53(3) | 4(2) | 5(2) | 6(2) |
| C(32) | 43(2) | 42(3) | 55(3) | -2(2) | -1(2) | 5(2) |
| C(33) | 47(3) | 98(5) | 62(3) | -13(3) | -3(3) | 1(3) |
| C(34) | 66(4) | 121(6) | 49(3) | -9(3) | -2(3) | 0(4) |
| C(35) | 45(3) | 38(3) | 70(3) | 5(2) | 6(2) | -1(2) |
| C(36) | 39(2) | 34(2) | 75(3) | 9(2) | 14(2) | -1(2) |
| C(37) | 41(3) | 37(3) | 98(4) | 4(3) | 17(3) | -2(2) |
| C(38) | 48(3) | 49(3) | 82(4) | 5(3) | 8(3) | 7(2) |
| C(39) | 46(3) | 55(3) | 72(4) | 7(3) | 3(2) | 2(2) |
| C(40) | 34(2) | 44(3) | 78(4) | 17(2) | 6(2) | 1(2) |
| C(41) | 57(3) | 74(4) | 82(4) | 22(3) | 12(3) | 15(3) |
| C(42) | 88(5) | 83(5) | 68(4) | 12(3) | -5(3) | 2(4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(43) | 56(3) | 56(3) | 51(3) | 14(2) | 1(2) | -7(2) |
| C(44) | 42(2) | 48(3) | 54(3) | 8(2) | 1(2) | -2(2) |
| C(45) | 40(2) | 49(3) | 46(2) | 7(2) | 2(2) | -4(2) |
| C(46) | 38(2) | 48(3) | 54(3) | 5(2) | 12(2) | -3(2) |
| C(47) | 89(4) | 53(3) | 54(3) | 0(2) | 20(3) | -12(3) |
| C(48) | 112(5) | 74(4) | 42(3) | 5(3) | 12(3) | -13(4) |
| C(49) | 38(2) | 47(3) | 60(3) | 9(2) | 10(2) | 0(2) |
| C(50) | 32(2) | 43(3) | 72(3) | 18(2) | 4(2) | 3(2) |
| C(51) | 38(2) | 45(3) | 99(4) | 29(3) | 15(3) | 9(2) |
| C(52) | 44(3) | 57(3) | 80(4) | 10(3) | 14(3) | -1(2) |
| C(53) | 54(3) | 49(3) | 65(3) | 8(2) | 7(2) | 1(2) |
| C(54) | 34(2) | 38(3) | 72(3) | 11(2) | -2(2) | 1(2) |
| C(55) | 77(4) | 96(5) | 67(4) | -2(4) | 1(3) | 5(4) |
| C(56) | 61(3) | 62(4) | 79(4) | 17(3) | -9(3) | -14(3) |

Table C.5v Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for ydbcl2m.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 7250(70) | 4090(80) | 4240(20) | 110(30) |
| H(4) | 5990(90) | 2850(60) | 800(30) | 120(30) |
| H(7) | 1130(100) | 2930(60) | 810(30) | 130(30) |
| H(10) | 7050(50) | 8980(50) | 4134(16) | 49(14) |
| H(2) | 9138 | 7668 | 3582 | 61 |
| H(3) | 8946 | 5882 | 4010 | 56 |
| H(5) | 8254 | 2773 | 3022 | 91 |
| H(6) | 8517 | 4552 | 2596 | 105 |
| H(7A) | 7791 | 2186 | 3690 | 62 |
| H(9A) | 11644 | 3796 | 3960 | 69 |
| H(9B) | 10691 | 4082 | 4335 | 69 |
| H(10A) | 12830 | 1840 | 4256 | 73 |
| H(10B) | 13084 | 3349 | 4558 | 73 |
| H(11) | 12400 | 1319 | 4869 | 67 |
| H(13A) | 11414 | 815 | 3621 | 100 |
| H(13B) | 10765 | 2066 | 3369 | 100 |
| H(13C) | 9771 | 680 | 3406 | 100 |
| H(14A) | 10332 | 3536 | 4993 | 128 |
| H(14B) | 11963 | 3626 | 5218 | 128 |
| H(14C) | 10851 | 2393 | 5298 | 128 |
| H(16) | 2249 | 5469 | 1434 | 61 |
| H(17) | 4051 | 4893 | 996 | 53 |
| H(19) | 7067 | 4923 | 1979 | 81 |

| | | | | |
|---|---|---|---|---|
| H(20) | 5289 | 5429 | 2409 | 88 |
| H(21) | 7714 | 3931 | 1305 | 55 |
| H(23A) | 5862 | 6314 | 681 | 73 |
| H(23B) | 6185 | 7599 | 1054 | 73 |
| H(24A) | 6613 | 8451 | 445 | 76 |
| H(24B) | 8109 | 8496 | 742 | 76 |
| H(25) | 8668 | 7504 | 134 | 69 |
| H(27A) | 9181 | 6144 | 1609 | 104 |
| H(27B) | 7842 | 7236 | 1638 | 104 |
| H(27C) | 9163 | 7586 | 1392 | 104 |
| H(28A) | 7613 | 5547 | -290 | 124 |
| H(28B) | 6414 | 6775 | -219 | 124 |
| H(28C) | 6415 | 5366 | 12 | 124 |
| H(30) | -2750 | 838 | 1406 | 60 |
| H(31) | -922 | 1109 | 991 | 56 |
| H(33) | 2046 | 1851 | 1984 | 86 |
| H(34) | 240 | 1563 | 2402 | 97 |
| H(35) | 2744 | 2268 | 1321 | 61 |
| H(37A) | 1159 | -1612 | 1043 | 70 |
| H(37B) | 864 | -670 | 675 | 70 |
| H(38A) | 3111 | -2814 | 728 | 72 |
| H(38B) | 1613 | -3067 | 431 | 72 |
| H(39) | 3650 | -2389 | 113 | 70 |
| H(41A) | 4168 | -1308 | 1374 | 104 |
| H(41B) | 2818 | -795 | 1617 | 104 |
| H(41C) | 4146 | 316 | 1612 | 104 |
| H(42A) | 1446 | -317 | 25 | 121 |
| H(42B) | 1385 | -1932 | -221 | 121 |
| H(42C) | 2610 | -787 | -287 | 121 |
| H(44) | 4654 | 12646 | 3597 | 58 |
| H(45) | 5232 | 10820 | 4005 | 54 |
| H(47) | 4991 | 7788 | 3000 | 78 |
| H(48) | 4329 | 9616 | 2590 | 91 |
| H(49) | 6050 | 7141 | 3663 | 58 |
| H(51A) | 3735 | 9074 | 4319 | 70 |
| H(51B) | 2447 | 8752 | 3953 | 70 |
| H(52A) | 1575 | 8377 | 4568 | 72 |
| H(52B) | 1522 | 6856 | 4270 | 72 |
| H(53) | 2500 | 6338 | 4876 | 67 |
| H(55A) | 4488 | 7391 | 5281 | 123 |
| H(55B) | 3238 | 8572 | 5232 | 123 |
| H(55C) | 4622 | 8591 | 4983 | 123 |
| H(56A) | 3840 | 5599 | 3404 | 102 |
| H(56B) | 2886 | 7021 | 3353 | 102 |
| H(56C) | 2363 | 5821 | 3612 | 102 |

Table C.6v Torsion angles [deg] for ydbcl2m.

| | |
|---|---|
| C(6)-C(1)-C(2)-C(3) | -0.2(9) |
| Cl(1)-C(1)-C(2)-C(3) | 179.5(4) |
| C(1)-C(2)-C(3)-C(4) | 0.2(7) |
| C(2)-C(3)-C(4)-C(5) | -1.3(7) |
| C(2)-C(3)-C(4)-C(7) | 178.7(4) |
| C(3)-C(4)-C(5)-C(6) | 2.3(10) |
| C(7)-C(4)-C(5)-C(6) | -177.7(6) |
| C(2)-C(1)-C(6)-C(5) | 1.2(11) |
| Cl(1)-C(1)-C(6)-C(5) | -178.5(6) |
| C(4)-C(5)-C(6)-C(1) | -2.3(12) |
| C(3)-C(4)-C(7)-O(1) | 25.7(6) |
| C(5)-C(4)-C(7)-O(1) | -154.3(5) |
| C(3)-C(4)-C(7)-C(8) | -93.8(6) |
| C(5)-C(4)-C(7)-C(8) | 86.3(6) |
| O(1)-C(7)-C(8)-C(13) | 172.3(4) |
| C(4)-C(7)-C(8)-C(13) | -63.7(6) |
| O(1)-C(7)-C(8)-C(12) | 57.0(5) |
| C(4)-C(7)-C(8)-C(12) | -179.0(4) |
| O(1)-C(7)-C(8)-C(9) | -64.0(5) |
| C(4)-C(7)-C(8)-C(9) | 60.0(6) |
| C(13)-C(8)-C(9)-C(10) | -82.2(6) |
| C(12)-C(8)-C(9)-C(10) | 37.3(6) |
| C(7)-C(8)-C(9)-C(10) | 154.2(5) |
| C(8)-C(9)-C(10)-C(11) | -61.7(6) |
| C(12)-O(2)-C(11)-C(10) | -21.2(7) |
| C(12)-O(2)-C(11)-C(14) | 110.5(6) |
| C(9)-C(10)-C(11)-O(2) | 52.8(6) |
| C(9)-C(10)-C(11)-C(14) | -73.7(7) |
| C(11)-O(2)-C(12)-O(3) | 174.2(5) |
| C(11)-O(2)-C(12)-C(8) | -3.2(7) |
| C(13)-C(8)-C(12)-O(3) | -60.5(6) |
| C(9)-C(8)-C(12)-O(3) | 177.5(5) |
| C(7)-C(8)-C(12)-O(3) | 57.7(6) |
| C(13)-C(8)-C(12)-O(2) | 116.8(5) |
| C(9)-C(8)-C(12)-O(2) | -5.1(7) |
| C(7)-C(8)-C(12)-O(2) | -124.9(5) |
| C(20)-C(15)-C(16)-C(17) | -1.4(9) |
| Cl(2)-C(15)-C(16)-C(17) | 179.5(4) |
| C(15)-C(16)-C(17)-C(18) | -0.5(7) |
| C(16)-C(17)-C(18)-C(19) | 1.4(7) |
| C(16)-C(17)-C(18)-C(21) | -178.5(4) |
| C(17)-C(18)-C(19)-C(20) | -0.6(9) |

| | |
|---|---|
| C(21)-C(18)-C(19)-C(20) | 179.4(6) |
| C(18)-C(19)-C(20)-C(15) | -1.2(11) |
| C(16)-C(15)-C(20)-C(19) | 2.3(10) |
| Cl(2)-C(15)-C(20)-C(19) | -178.7(6) |
| C(19)-C(18)-C(21)-O(4) | 152.6(5) |
| C(17)-C(18)-C(21)-O(4) | -27.5(6) |
| C(19)-C(18)-C(21)-C(22) | -88.3(6) |
| C(17)-C(18)-C(21)-C(22) | 91.6(6) |
| O(4)-C(21)-C(22)-C(26) | -57.5(5) |
| C(18)-C(21)-C(22)-C(26) | 178.4(4) |
| O(4)-C(21)-C(22)-C(27) | -172.3(4) |
| C(18)-C(21)-C(22)-C(27) | 63.6(6) |
| O(4)-C(21)-C(22)-C(23) | 64.1(5) |
| C(18)-C(21)-C(22)-C(23) | -60.0(6) |
| C(26)-C(22)-C(23)-C(24) | -34.8(7) |
| C(27)-C(22)-C(23)-C(24) | 84.1(6) |
| C(21)-C(22)-C(23)-C(24) | -152.6(5) |
| C(22)-C(23)-C(24)-C(25) | 59.6(7) |
| C(26)-O(5)-C(25)-C(24) | 21.8(7) |
| C(26)-O(5)-C(25)-C(28) | -110.5(6) |
| C(23)-C(24)-C(25)-O(5) | -52.3(6) |
| C(23)-C(24)-C(25)-C(28) | 75.3(7) |
| C(25)-O(5)-C(26)-O(6) | -174.8(5) |
| C(25)-O(5)-C(26)-C(22) | 3.2(7) |
| C(27)-C(22)-C(26)-O(6) | 60.0(6) |
| C(23)-C(22)-C(26)-O(6) | -178.5(5) |
| C(21)-C(22)-C(26)-O(6) | -57.6(6) |
| C(27)-C(22)-C(26)-O(5) | -118.0(5) |
| C(23)-C(22)-C(26)-O(5) | 3.5(6) |
| C(21)-C(22)-C(26)-O(5) | 124.4(5) |
| C(34)-C(29)-C(30)-C(31) | 0.9(9) |
| Cl(3)-C(29)-C(30)-C(31) | -178.2(4) |
| C(29)-C(30)-C(31)-C(32) | 1.2(8) |
| C(30)-C(31)-C(32)-C(33) | -3.6(8) |
| C(30)-C(31)-C(32)-C(35) | 177.3(5) |
| C(31)-C(32)-C(33)-C(34) | 3.9(10) |
| C(35)-C(32)-C(33)-C(34) | -177.0(6) |
| C(32)-C(33)-C(34)-C(29) | -1.9(12) |
| C(30)-C(29)-C(34)-C(33) | -0.6(11) |
| Cl(3)-C(29)-C(34)-C(33) | 178.5(6) |
| C(33)-C(32)-C(35)-O(7) | -153.8(5) |
| C(31)-C(32)-C(35)-O(7) | 25.3(7) |
| C(33)-C(32)-C(35)-C(36) | 87.5(6) |
| C(31)-C(32)-C(35)-C(36) | -93.4(6) |
| O(7)-C(35)-C(36)-C(40) | 56.9(5) |
| C(32)-C(35)-C(36)-C(40) | -179.3(4) |

| | |
|---|---|
| O(7)-C(35)-C(36)-C(41) | 172.5(4) |
| C(32)-C(35)-C(36)-C(41) | -63.7(6) |
| O(7)-C(35)-C(36)-C(37) | -64.9(5) |
| C(32)-C(35)-C(36)-C(37) | 58.9(6) |
| C(40)-C(36)-C(37)-C(38) | 35.5(6) |
| C(41)-C(36)-C(37)-C(38) | -83.5(6) |
| C(35)-C(36)-C(37)-C(38) | 153.4(5) |
| C(36)-C(37)-C(38)-C(39) | -60.9(6) |
| C(40)-O(8)-C(39)-C(42) | 108.7(6) |
| C(40)-O(8)-C(39)-C(38) | -22.5(7) |
| C(37)-C(38)-C(39)-C(42) | -72.8(7) |
| C(37)-C(38)-C(39)-O(8) | 53.1(6) |
| C(39)-O(8)-C(40)-O(9) | 175.6(5) |
| C(39)-O(8)-C(40)-C(36) | -2.9(8) |
| C(41)-C(36)-C(40)-O(9) | -61.4(6) |
| C(37)-C(36)-C(40)-O(9) | 177.6(5) |
| C(35)-C(36)-C(40)-O(9) | 56.9(6) |
| C(41)-C(36)-C(40)-O(8) | 117.0(5) |
| C(37)-C(36)-C(40)-O(8) | -4.0(7) |
| C(35)-C(36)-C(40)-O(8) | -124.6(5) |
| C(48)-C(43)-C(44)-C(45) | -0.9(8) |
| Cl(4)-C(43)-C(44)-C(45) | 178.4(4) |
| C(43)-C(44)-C(45)-C(46) | 0.2(7) |
| C(44)-C(45)-C(46)-C(47) | 1.7(7) |
| C(44)-C(45)-C(46)-C(49) | -178.0(4) |
| C(45)-C(46)-C(47)-C(48) | -2.9(9) |
| C(49)-C(46)-C(47)-C(48) | 176.9(6) |
| C(44)-C(43)-C(48)-C(47) | -0.2(10) |
| Cl(4)-C(43)-C(48)-C(47) | -179.6(5) |
| C(46)-C(47)-C(48)-C(43) | 2.2(10) |
| C(45)-C(46)-C(49)-O(10) | -25.9(6) |
| C(47)-C(46)-C(49)-O(10) | 154.4(5) |
| C(45)-C(46)-C(49)-C(50) | 93.3(6) |
| C(47)-C(46)-C(49)-C(50) | -86.4(6) |
| O(10)-C(49)-C(50)-C(56) | -171.4(4) |
| C(46)-C(49)-C(50)-C(56) | 65.0(6) |
| O(10)-C(49)-C(50)-C(54) | -55.4(5) |
| C(46)-C(49)-C(50)-C(54) | -178.9(4) |
| O(10)-C(49)-C(50)-C(51) | 65.4(5) |
| C(46)-C(49)-C(50)-C(51) | -58.1(6) |
| C(56)-C(50)-C(51)-C(52) | 84.0(6) |
| C(54)-C(50)-C(51)-C(52) | -36.0(6) |
| C(49)-C(50)-C(51)-C(52) | -153.5(5) |
| C(50)-C(51)-C(52)-C(53) | 60.3(6) |
| C(54)-O(11)-C(53)-C(55) | -110.5(6) |
| C(54)-O(11)-C(53)-C(52) | 21.8(7) |

| | |
|---|---|
| C(51)-C(52)-C(53)-O(11) | -52.3(6) |
| C(51)-C(52)-C(53)-C(55) | 75.3(7) |
| C(53)-O(11)-C(54)-O(12) | -175.8(5) |
| C(53)-O(11)-C(54)-C(50) | 2.4(7) |
| C(56)-C(50)-C(54)-O(12) | 60.8(6) |
| C(49)-C(50)-C(54)-O(12) | -57.1(6) |
| C(51)-C(50)-C(54)-O(12) | -177.0(4) |
| C(56)-C(50)-C(54)-O(11) | -117.4(5) |
| C(49)-C(50)-C(54)-O(11) | 124.7(5) |
| C(51)-C(50)-C(54)-O(11) | 4.8(6) |

Table C.7v Hydrogen bonds for ydbcl2m [A and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(1)-H(1)...O(12) | 0.94(4) | 1.91(5) | 2.800(5) | 158(7) |
| O(4)-H(4)...O(9) | 0.94(4) | 1.86(5) | 2.786(5) | 168(8) |
| O(7)-H(7)...O(6)#1 | 0.93(4) | 1.88(5) | 2.782(5) | 163(9) |
| O(10)-H(10)...O(3)#2 | 0.94(4) | 1.86(4) | 2.787(5) | 172(5) |

Symmetry transformations used to generate equivalent atoms:
#1 x-1,y,z #2 x,y+1,z

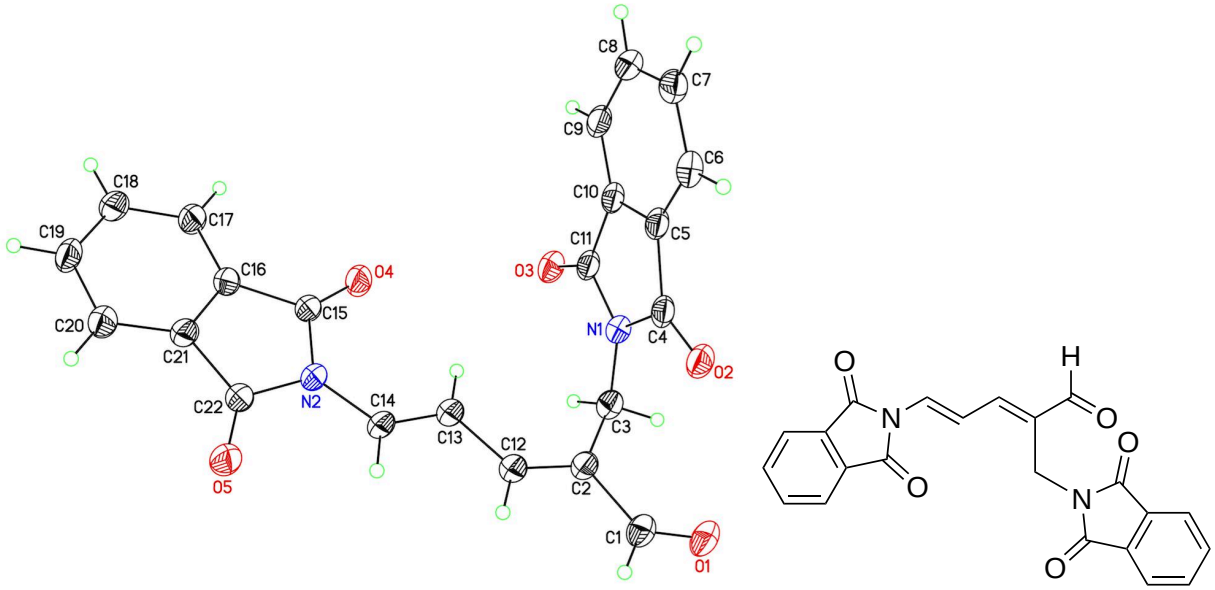


Figure C.23 Structure of nphth2.

**Structure Determination.**

Yellow needles of **nphth2** were grown from a dichloromethane/hexanes solution of the compound at 22 deg. C. A crystal of dimensions 0.10 x 0.03 x 0.03 mm was mounted on a

Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ω. The exposure times were 1 sec. for the low angle images, 6 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 13151 reflections to a maximum 2θ value of 136.48° of which 3154 were independent and 2797 were greater than 2σ(I). The final cell constants (Table 1) were based on the xyz centroids 5798 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group P1bar with Z = 2 for the formula $C_{22}H_{14}N_2O_5$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. The aldehyde group is rotationally disordered in two orientations. Full matrix least-squares refinement based on $F^2$ converged at R1 = 0.0412 and wR2 = 0.1112 [based on I > 2sigma(I)], R1 = 0.0460 and wR2 = 0.1166 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Sheldrick, G.M. SHELXTL, v. 2014/6; Bruker Analytical X-ray, Madison, WI, 2014.

CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015).

Table C.1w Crystal data and structure refinement for nphth2.

| | |
|---|---|
| Identification code | nphth2 |
| Empirical formula | C22 H14 N2 O5 |
| Formula weight | 386.35 |
| Temperature | 85(2) K |
| Wavelength | 1.54184 A |
| Crystal system, space group | Triclinic, P-1 |
| Unit cell dimensions | a = 5.5524(2) A alpha = 103.452(3) deg. |
| | b = 10.0967(4) A beta = 97.125(3) deg. |
| | c = 16.2260(5) A gamma = 95.756(3) deg. |
| Volume | 869.96(6) A^3 |
| Z, Calculated density | 2, 1.475 Mg/m^3 |
| Absorption coefficient | 0.886 mm^-1 |
| F(000) | 400 |
| Crystal size | 0.100 x 0.030 x 0.030 mm |
| Theta range for data collection | 2.833 to 69.243 deg. |
| Limiting indices | -6<=h<=6, -10<=k<=12, -19<=l<=19 |
| Reflections collected / unique | 13151 / 3154 [R(int) = 0.0418] |
| Completeness to theta = 67.684 | 97.6 % |

| | |
|---|---|
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00000 and 0.91484 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 3154 / 251 / 281 |
| Goodness-of-fit on F^2 | 1.035 |
| Final R indices [I>2sigma(I)] | R1 = 0.0412, wR2 = 0.1112 |
| R indices (all data) | R1 = 0.0460, wR2 = 0.1166 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.177 and -0.226 e.A^-3 |

Table C.2w Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for nphth2. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 7546(3) | 9104(1) | 8702(1) | 38(1) |
| O(1A) | 9720(20) | 8729(17) | 7925(11) | 56(5) |
| O(2) | 7982(2) | 6002(1) | 9168(1) | 31(1) |
| O(3) | 316(2) | 4257(1) | 7693(1) | 31(1) |
| O(4) | 2319(2) | 2347(1) | 5648(1) | 34(1) |
| O(5) | 8782(2) | 3170(1) | 4240(1) | 34(1) |
| N(1) | 4145(2) | 5408(1) | 8344(1) | 25(1) |
| N(2) | 5790(2) | 3077(1) | 5116(1) | 26(1) |
| C(1) | 7831(7) | 8293(5) | 8073(4) | 30(1) |
| C(1A) | 8250(70) | 8140(50) | 8060(40) | 24(6) |
| C(2) | 6269(3) | 6993(2) | 7634(1) | 26(1) |
| C(3) | 4035(3) | 6632(2) | 8014(1) | 28(1) |
| C(4) | 6123(3) | 5197(2) | 8902(1) | 26(1) |
| C(5) | 5413(3) | 3845(2) | 9080(1) | 26(1) |
| C(6) | 6713(3) | 3119(2) | 9565(1) | 29(1) |
| C(7) | 5548(3) | 1857(2) | 9614(1) | 32(1) |
| C(8) | 3154(3) | 1363(2) | 9209(1) | 32(1) |
| C(9) | 1870(3) | 2099(2) | 8718(1) | 29(1) |
| C(10) | 3041(3) | 3336(2) | 8658(1) | 26(1) |
| C(11) | 2223(3) | 4328(2) | 8168(1) | 26(1) |
| C(12) | 6942(3) | 6232(2) | 6919(1) | 27(1) |
| C(13) | 5687(3) | 4938(2) | 6382(1) | 26(1) |
| C(14) | 6700(3) | 4333(2) | 5706(1) | 26(1) |
| C(15) | 3695(3) | 2166(2) | 5124(1) | 26(1) |
| C(16) | 3608(3) | 984(2) | 4370(1) | 26(1) |
| C(17) | 1965(3) | -209(2) | 4084(1) | 30(1) |
| C(18) | 2375(3) | -1169(2) | 3362(1) | 31(1) |
| C(19) | 4335(3) | -925(2) | 2940(1) | 31(1) |

| | | | | |
|---|---|---|---|---|
| C(20) | 5985(3) | 280(2) | 3227(1) | 30(1) |
| C(21) | 5575(3) | 1217(2) | 3951(1) | 26(1) |
| C(22) | 6985(3) | 2571(2) | 4410(1) | 25(1) |

Table C.3w Bond lengths [A] and angles [deg] for nphth2.

| | |
|---|---|
| O(1)-C(1) | 1.190(4) |
| O(1A)-C(1A) | 1.04(4) |
| O(2)-C(4) | 1.212(2) |
| O(3)-C(11) | 1.2151(19) |
| O(4)-C(15) | 1.2062(19) |
| O(5)-C(22) | 1.209(2) |
| N(1)-C(11) | 1.398(2) |
| N(1)-C(4) | 1.401(2) |
| N(1)-C(3) | 1.461(2) |
| N(2)-C(14) | 1.403(2) |
| N(2)-C(15) | 1.412(2) |
| N(2)-C(22) | 1.413(2) |
| C(1)-C(2) | 1.471(3) |
| C(1)-H(1) | 0.9500 |
| C(1A)-C(2) | 1.486(18) |
| C(1A)-H(1A) | 0.9500 |
| C(2)-C(12) | 1.351(2) |
| C(2)-C(3) | 1.502(2) |
| C(3)-H(3A) | 0.9900 |
| C(3)-H(3B) | 0.9900 |
| C(4)-C(5) | 1.485(2) |
| C(5)-C(6) | 1.383(2) |
| C(5)-C(10) | 1.394(2) |
| C(6)-C(7) | 1.394(3) |
| C(6)-H(6) | 0.9500 |
| C(7)-C(8) | 1.395(2) |
| C(7)-H(7) | 0.9500 |
| C(8)-C(9) | 1.391(2) |
| C(8)-H(8) | 0.9500 |
| C(9)-C(10) | 1.380(2) |
| C(9)-H(9) | 0.9500 |
| C(10)-C(11) | 1.488(2) |
| C(12)-C(13) | 1.445(2) |
| C(12)-H(12) | 0.9500 |
| C(13)-C(14) | 1.342(2) |
| C(13)-H(13) | 0.9500 |
| C(14)-H(14) | 0.9500 |
| C(15)-C(16) | 1.489(2) |

| | |
|---|---|
| C(16)-C(17) | 1.383(2) |
| C(16)-C(21) | 1.385(2) |
| C(17)-C(18) | 1.394(2) |
| C(17)-H(17) | 0.9500 |
| C(18)-C(19) | 1.387(2) |
| C(18)-H(18) | 0.9500 |
| C(19)-C(20) | 1.394(2) |
| C(19)-H(19) | 0.9500 |
| C(20)-C(21) | 1.386(2) |
| C(20)-H(20) | 0.9500 |
| C(21)-C(22) | 1.484(2) |
| C(11)-N(1)-C(4) | 111.82(13) |
| C(11)-N(1)-C(3) | 123.58(13) |
| C(4)-N(1)-C(3) | 124.55(13) |
| C(14)-N(2)-C(15) | 127.59(13) |
| C(14)-N(2)-C(22) | 121.07(13) |
| C(15)-N(2)-C(22) | 111.33(12) |
| O(1)-C(1)-C(2) | 127.7(3) |
| O(1)-C(1)-H(1) | 116.1 |
| C(2)-C(1)-H(1) | 116.1 |
| O(1A)-C(1A)-C(2) | 141(5) |
| O(1A)-C(1A)-H(1A) | 109.4 |
| C(2)-C(1A)-H(1A) | 109.4 |
| C(12)-C(2)-C(1) | 117.5(2) |
| C(12)-C(2)-C(1A) | 109.6(19) |
| C(12)-C(2)-C(3) | 125.39(15) |
| C(1)-C(2)-C(3) | 117.1(2) |
| C(1A)-C(2)-C(3) | 124(2) |
| N(1)-C(3)-C(2) | 112.93(13) |
| N(1)-C(3)-H(3A) | 109.0 |
| C(2)-C(3)-H(3A) | 109.0 |
| N(1)-C(3)-H(3B) | 109.0 |
| C(2)-C(3)-H(3B) | 109.0 |
| H(3A)-C(3)-H(3B) | 107.8 |
| O(2)-C(4)-N(1) | 124.36(15) |
| O(2)-C(4)-C(5) | 129.81(15) |
| N(1)-C(4)-C(5) | 105.83(13) |
| C(6)-C(5)-C(10) | 121.40(16) |
| C(6)-C(5)-C(4) | 130.19(15) |
| C(10)-C(5)-C(4) | 108.40(14) |
| C(5)-C(6)-C(7) | 117.09(15) |
| C(5)-C(6)-H(6) | 121.5 |
| C(7)-C(6)-H(6) | 121.5 |
| C(6)-C(7)-C(8) | 121.50(16) |
| C(6)-C(7)-H(7) | 119.3 |
| C(8)-C(7)-H(7) | 119.3 |

| | |
|---|---|
| C(9)-C(8)-C(7) | 120.88(16) |
| C(9)-C(8)-H(8) | 119.6 |
| C(7)-C(8)-H(8) | 119.6 |
| C(10)-C(9)-C(8) | 117.53(15) |
| C(10)-C(9)-H(9) | 121.2 |
| C(8)-C(9)-H(9) | 121.2 |
| C(9)-C(10)-C(5) | 121.56(15) |
| C(9)-C(10)-C(11) | 130.67(14) |
| C(5)-C(10)-C(11) | 107.75(14) |
| O(3)-C(11)-N(1) | 124.64(15) |
| O(3)-C(11)-C(10) | 129.22(15) |
| N(1)-C(11)-C(10) | 106.13(12) |
| C(2)-C(12)-C(13) | 127.24(15) |
| C(2)-C(12)-H(12) | 116.4 |
| C(13)-C(12)-H(12) | 116.4 |
| C(14)-C(13)-C(12) | 117.68(15) |
| C(14)-C(13)-H(13) | 121.2 |
| C(12)-C(13)-H(13) | 121.2 |
| C(13)-C(14)-N(2) | 126.47(15) |
| C(13)-C(14)-H(14) | 116.8 |
| N(2)-C(14)-H(14) | 116.8 |
| O(4)-C(15)-N(2) | 125.47(14) |
| O(4)-C(15)-C(16) | 129.10(15) |
| N(2)-C(15)-C(16) | 105.43(13) |
| C(17)-C(16)-C(21) | 121.12(15) |
| C(17)-C(16)-C(15) | 129.95(15) |
| C(21)-C(16)-C(15) | 108.92(14) |
| C(16)-C(17)-C(18) | 117.51(15) |
| C(16)-C(17)-H(17) | 121.2 |
| C(18)-C(17)-H(17) | 121.2 |
| C(19)-C(18)-C(17) | 121.19(15) |
| C(19)-C(18)-H(18) | 119.4 |
| C(17)-C(18)-H(18) | 119.4 |
| C(18)-C(19)-C(20) | 121.30(15) |
| C(18)-C(19)-H(19) | 119.4 |
| C(20)-C(19)-H(19) | 119.4 |
| C(21)-C(20)-C(19) | 116.93(15) |
| C(21)-C(20)-H(20) | 121.5 |
| C(19)-C(20)-H(20) | 121.5 |
| C(16)-C(21)-C(20) | 121.94(15) |
| C(16)-C(21)-C(22) | 108.23(13) |
| C(20)-C(21)-C(22) | 129.83(15) |
| O(5)-C(22)-N(2) | 124.66(14) |
| O(5)-C(22)-C(21) | 129.27(15) |
| N(2)-C(22)-C(21) | 106.06(13) |

Table C.4w Anisotropic displacement parameters (A^2 x 10^3) for nphth2. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| O(1) | 47(1) | 26(1) | 34(1) | -5(1) | 4(1) | -1(1) |
| O(1A) | 44(6) | 50(7) | 66(10) | 6(7) | 14(6) | -15(5) |
| O(2) | 30(1) | 29(1) | 25(1) | -1(1) | 0(1) | -4(1) |
| O(3) | 31(1) | 29(1) | 28(1) | 0(1) | -4(1) | 0(1) |
| O(4) | 37(1) | 33(1) | 27(1) | -2(1) | 10(1) | -9(1) |
| O(5) | 34(1) | 30(1) | 33(1) | 0(1) | 10(1) | -7(1) |
| N(1) | 28(1) | 22(1) | 22(1) | 2(1) | 2(1) | -1(1) |
| N(2) | 28(1) | 22(1) | 22(1) | 1(1) | 3(1) | -5(1) |
| C(1) | 34(2) | 24(1) | 29(1) | 2(1) | 1(1) | 3(1) |
| C(1A) | 21(7) | 16(8) | 33(7) | 2(5) | 0(5) | 8(7) |
| C(2) | 31(1) | 22(1) | 24(1) | 4(1) | 1(1) | 0(1) |
| C(3) | 33(1) | 23(1) | 26(1) | 2(1) | 4(1) | 3(1) |
| C(4) | 29(1) | 25(1) | 18(1) | -2(1) | 4(1) | 2(1) |
| C(5) | 30(1) | 24(1) | 19(1) | -2(1) | 4(1) | 1(1) |
| C(6) | 32(1) | 30(1) | 22(1) | -1(1) | 2(1) | 4(1) |
| C(7) | 43(1) | 28(1) | 24(1) | 2(1) | 4(1) | 7(1) |
| C(8) | 44(1) | 23(1) | 26(1) | 1(1) | 6(1) | 0(1) |
| C(9) | 34(1) | 25(1) | 24(1) | -2(1) | 4(1) | -1(1) |
| C(10) | 31(1) | 24(1) | 19(1) | -2(1) | 3(1) | 1(1) |
| C(11) | 30(1) | 23(1) | 21(1) | -2(1) | 4(1) | 1(1) |
| C(12) | 31(1) | 24(1) | 24(1) | 5(1) | 1(1) | -1(1) |
| C(13) | 30(1) | 23(1) | 24(1) | 4(1) | 1(1) | -3(1) |
| C(14) | 30(1) | 21(1) | 24(1) | 2(1) | 0(1) | -4(1) |
| C(15) | 29(1) | 24(1) | 22(1) | 3(1) | 3(1) | -5(1) |
| C(16) | 30(1) | 25(1) | 21(1) | 4(1) | 1(1) | -2(1) |
| C(17) | 32(1) | 28(1) | 25(1) | 2(1) | 3(1) | -5(1) |
| C(18) | 35(1) | 26(1) | 26(1) | 2(1) | -1(1) | -5(1) |
| C(19) | 36(1) | 25(1) | 26(1) | -2(1) | 2(1) | 1(1) |
| C(20) | 33(1) | 27(1) | 27(1) | 2(1) | 5(1) | 0(1) |
| C(21) | 28(1) | 23(1) | 23(1) | 4(1) | 1(1) | -1(1) |
| C(22) | 27(1) | 24(1) | 23(1) | 4(1) | 3(1) | -1(1) |

Table C.5w Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for nphth2.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 9234 | 8510 | 7824 | 36 |
| H(1A) | 8122 | 8430 | 8649 | 29 |
| H(3A) | 3847 | 7417 | 8485 | 34 |
| H(3B) | 2572 | 6477 | 7570 | 34 |
| H(6) | 8330 | 3465 | 9852 | 35 |
| H(7) | 6405 | 1321 | 9930 | 39 |
| H(8) | 2391 | 513 | 9269 | 39 |
| H(9) | 247 | 1761 | 8435 | 35 |
| H(12) | 8403 | 6586 | 6751 | 32 |
| H(13) | 4198 | 4529 | 6503 | 32 |
| H(14) | 8181 | 4803 | 5619 | 32 |
| H(17) | 609 | -368 | 4368 | 36 |
| H(18) | 1292 | -2004 | 3156 | 37 |
| H(19) | 4557 | -1593 | 2446 | 37 |
| H(20) | 7327 | 451 | 2939 | 36 |

Table C.6w Torsion angles [deg] for nphth2.

| | |
|---|---|
| O(1)-C(1)-C(2)-C(12) | 179.5(6) |
| O(1)-C(1)-C(2)-C(3) | 0.2(9) |
| O(1A)-C(1A)-C(2)-C(12) | 24(10) |
| O(1A)-C(1A)-C(2)-C(3) | -164(7) |
| C(11)-N(1)-C(3)-C(2) | -132.47(15) |
| C(4)-N(1)-C(3)-C(2) | 50.49(19) |
| C(12)-C(2)-C(3)-N(1) | 66.4(2) |
| C(1)-C(2)-C(3)-N(1) | -114.4(4) |
| C(1A)-C(2)-C(3)-N(1) | -104(4) |
| C(11)-N(1)-C(4)-O(2) | -178.13(14) |
| C(3)-N(1)-C(4)-O(2) | -0.8(2) |
| C(11)-N(1)-C(4)-C(5) | 1.41(16) |
| C(3)-N(1)-C(4)-C(5) | 178.76(13) |
| O(2)-C(4)-C(5)-C(6) | -3.0(3) |
| N(1)-C(4)-C(5)-C(6) | 177.53(15) |
| O(2)-C(4)-C(5)-C(10) | 177.06(15) |
| N(1)-C(4)-C(5)-C(10) | -2.45(16) |
| C(10)-C(5)-C(6)-C(7) | 0.0(2) |
| C(4)-C(5)-C(6)-C(7) | -179.98(15) |
| C(5)-C(6)-C(7)-C(8) | -1.5(2) |
| C(6)-C(7)-C(8)-C(9) | 2.0(2) |
| C(7)-C(8)-C(9)-C(10) | -0.9(2) |
| C(8)-C(9)-C(10)-C(5) | -0.7(2) |
| C(8)-C(9)-C(10)-C(11) | 177.57(15) |

| | |
|---|---|
| C(6)-C(5)-C(10)-C(9) | 1.1(2) |
| C(4)-C(5)-C(10)-C(9) | -178.88(13) |
| C(6)-C(5)-C(10)-C(11) | -177.47(14) |
| C(4)-C(5)-C(10)-C(11) | 2.51(16) |
| C(4)-N(1)-C(11)-O(3) | -178.92(14) |
| C(3)-N(1)-C(11)-O(3) | 3.7(2) |
| C(4)-N(1)-C(11)-C(10) | 0.08(16) |
| C(3)-N(1)-C(11)-C(10) | -177.30(13) |
| C(9)-C(10)-C(11)-O(3) | -1.2(3) |
| C(5)-C(10)-C(11)-O(3) | 177.29(15) |
| C(9)-C(10)-C(11)-N(1) | 179.91(15) |
| C(5)-C(10)-C(11)-N(1) | -1.65(16) |
| C(1)-C(2)-C(12)-C(13) | -179.3(4) |
| C(1A)-C(2)-C(12)-C(13) | 172(3) |
| C(3)-C(2)-C(12)-C(13) | -0.1(3) |
| C(2)-C(12)-C(13)-C(14) | -178.69(15) |
| C(12)-C(13)-C(14)-N(2) | 179.32(14) |
| C(15)-N(2)-C(14)-C(13) | -2.6(3) |
| C(22)-N(2)-C(14)-C(13) | 177.73(15) |
| C(14)-N(2)-C(15)-O(4) | 1.1(3) |
| C(22)-N(2)-C(15)-O(4) | -179.21(16) |
| C(14)-N(2)-C(15)-C(16) | -178.53(14) |
| C(22)-N(2)-C(15)-C(16) | 1.15(17) |
| O(4)-C(15)-C(16)-C(17) | -0.8(3) |
| N(2)-C(15)-C(16)-C(17) | 178.78(16) |
| O(4)-C(15)-C(16)-C(21) | -179.74(16) |
| N(2)-C(15)-C(16)-C(21) | -0.12(17) |
| C(21)-C(16)-C(17)-C(18) | 0.5(2) |
| C(15)-C(16)-C(17)-C(18) | -178.31(15) |
| C(16)-C(17)-C(18)-C(19) | -1.0(2) |
| C(17)-C(18)-C(19)-C(20) | 0.7(3) |
| C(18)-C(19)-C(20)-C(21) | 0.1(2) |
| C(17)-C(16)-C(21)-C(20) | 0.4(2) |
| C(15)-C(16)-C(21)-C(20) | 179.40(14) |
| C(17)-C(16)-C(21)-C(22) | -179.90(14) |
| C(15)-C(16)-C(21)-C(22) | -0.88(17) |
| C(19)-C(20)-C(21)-C(16) | -0.7(2) |
| C(19)-C(20)-C(21)-C(22) | 179.68(15) |
| C(14)-N(2)-C(22)-O(5) | -2.5(2) |
| C(15)-N(2)-C(22)-O(5) | 177.78(15) |
| C(14)-N(2)-C(22)-C(21) | 178.03(13) |
| C(15)-N(2)-C(22)-C(21) | -1.68(17) |
| C(16)-C(21)-C(22)-O(5) | -177.87(16) |
| C(20)-C(21)-C(22)-O(5) | 1.8(3) |
| C(16)-C(21)-C(22)-N(2) | 1.56(17) |
| C(20)-C(21)-C(22)-N(2) | -178.76(15) |

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